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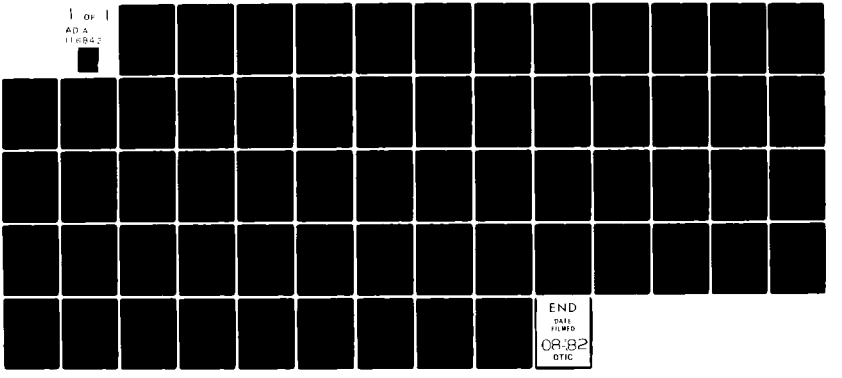

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FINAL REPORT

SUPERCRITICAL CARBON DIOXIDE REGENERATION OF ACTIVATED CARBON LOADED WITH CONTAMINANTS FROM ROCKY MOUNTAIN ARSENAL WELL WATER

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CONTRACT NUMBER DAAK70-79-D-0036 Task Order 0015

MAY 1982

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The method of supercritical carbon dioxide (SCF CO_2) regeneration of granular activated carbon (GAC) loaded with DIMP (diisopropyl methylphosphonate) from Rocky Mountain Arsenal Well (No. 23-120) water was investigated. A laboratory-based adsorption/regeneration study was done in two parts. Part one compared the performance of three commercially available granular activated carbons as adsorbents for DIMP using SCF CO_2 regeneration. Part two compared the effectiveness of SCF CO_2 regeneration

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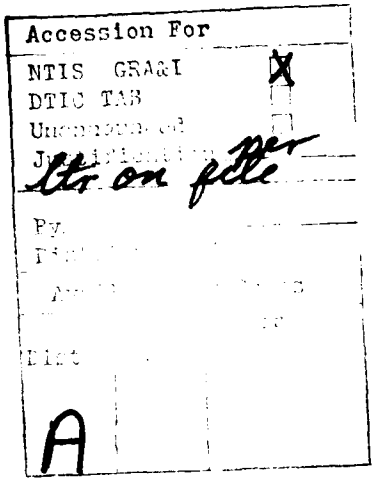
versus conventional thermal regeneration for one commercial GAC loaded with DIMP from RMA Well No. 23-120. Economic evaluations based on the test data for the SCF CO_2 regeneration system and for a conventional thermal regeneration system were made. Results indicated that thermal regeneration outperformed the supercritical process in restoring carbon capacity for DIMP. Results of the economic evaluation also indicated that the cost of the carbon regeneration step in the treatment of 600 GPM of RMA groundwater is $0.56 per 1000 gallons of water for the thermal process and $1.41 per 1000 gallons of water for the supercritical process.

Because the supercritical carbon dioxide process did not appear favorable, recommendations were made for further investigation to try to reduce the cost and increase the efficiency of the supercritical process.

FOREWARD

This work was performed under the sponsorship of the U.S. Army Mobility Equipment Research and Development Command (MERADCOM). The work was performed by Arthur D. Little, Inc. of Cambridge, Ma. 02140 under Task Order 0015 of Contract Number DAAK70-79-D-0036. Portions of the experimental work were performed under subcontract to Rubel and Hager, Inc. of Tucson, Arizona (ADL P.O. No. 445648). Ms. Rosemary Murphy O'Brien and Dr. Richard P. de Filippi of Arthur D. Little, and Mr. Clinton E. Smith and Donald G. Hager were the authors. This report was prepared under the guidance of Mr. Edward Colburn of the U.S. Army Toxic and Hazardous Materials Agency, Edgewood Area, APG, Md. 21010 as the technical point of contact and Mr. Jerry Dean of MERADCOM as the Contract Officer's Representative.



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I. INTRODUCTION AND OBJECTIVES

Rocky Mountain Arsenal groundwater has been contaminated with trace quantities of a variety of organic compounds. Currently there is an installation restoration program underway which includes the use of granular activated carbon (GAC) adsorption, since many of the contaminants can be adsorbed onto GAC. The degree and type of contamination varies throughout the arsenal area. Compounds such as DBCP (1,2-Dibromo-3-chloropropane or Nemagon), dicyclopentadiene, DIMP (diisopropyl methylphosphonate), and Endrin have been found in trace quantities [1]. DIMP is one of the most predominant of the organics present in the groundwater. These and other groundwater contaminants are known or suspected toxins [2,3] and must be removed from the area to avoid contaminated groundwater migration to areas other than the arsenal.

Adsorption on granular activated carbon (GAC) is a widely accepted method for removal of contaminants from water for both water and wastewater treatment. GAC is a broad base adsorbent, good for removal of a wide variety of compounds from aqueous solutions. The primary drawback to its use is its cost. The use of GAC is often economically feasible only if the exhausted, fully-loaded GAC can be regenerated for reuse. Usually, a large percentage of the virgin GAC capacity must be recovered over each subsequent cycle to keep replacement carbon costs to a minimum.

Methods of regeneration of GAC must be both effective in removing the adsorbed compound(s) (adsorbates) and be fairly inexpensive. Thermal regeneration of spent liquid phase GAC is the primary and, in some instances, the only method available. Although carbon may be thermally regenerated to regain very-near virgin capacity, carbon losses due to oxidation are ten percent or greater [4]. Another drawback is the large capital cost of a typical GAC thermal regeneration system, primarily the multiple-hearth furnace, and large associated energy costs.

The purpose of this project was to study the use of supercritical fluids to regenerate activated carbon applied to the adsorption of various organic contaminants from Rocky Mountain Arsenal Wellwater as an alternative to thermal methods of regeneration. Another objective was to perform an economic evaluation of a regeneration process using supercritical carbon dioxide and of a thermal regeneration process such as multiple hearth or fluidized bed furnace regeneration.

Prior studies at Arthur D. Little, Inc. have shown that supercritical fluids (fluids in the region of and above their critical temperatures and pressures) can rapidly and effectively regenerate adsorbents such as granular activated carbon loaded with a broad variety of organic adsorbates. This regeneration process uses a supercritical fluid (e.g., carbon dioxide above its critical temperature and pressure) to desorb organics from GAC used to decontaminate RMA groundwater. The spent GAC is charged to a high pressure desorption vessel and the

supercritical carbon dioxide is flowed through the GAC at conditions which favor the desorption of the organics from the GAC and into the carbon dioxide phase. The effluent regenerant stream is rendered subcritical by reducing its pressure and/or temperature and a separation of regenerant and desorbate is effected. The CO_2 is then recovered for recycle. The concentrated desorbate may then be destroyed or sent to a safe containment site.

There are several favorable properties of supercritical fluids which make them advantageous for a solvent regeneration process:

(1) The organic adsorbates are highly soluble in the supercritical fluid.

(2) The relative volatility of the supercritical fluid and organic is large, making their separation easy.

(3) The diffusivity of the supercritical fluid is high, and resistances to mass transfer are, in most cases, negligible [5].

Carbon dioxide is a particularly suitable solvent; its critical temperature and pressure (31.0°C and 72.8 atm) are economically attainable, it has high solubilities for organic compounds, it is fairly dense at process conditions (power requirements for compression are reasonable), and it is abundant, non-flammable and non-toxic.

II. PREVIOUS WORK WITH SUPERCRITICAL-FLUID REGENERATION OF GRANULAR ACTIVATED CARBON (GAC)

Arthur D. Little, Inc. has had several development programs to demonstrate supercritical carbon dioxide regeneration of a broad variety of adsorbents in the past four years. These programs have included regeneration of liquid-phase adsorbents (including both GAC and synthetic resins) and of vapor-phase adsorbents (GAC's). Both synthetic and actual adsorbate solutions have been tested.

A two-year developmental program [6] determined that supercritical carbon dioxide could effectively regenerate liquid phase adsorbents (commercial GAC's, developmental GAC, commercial powdered activated carbon and commercial synthetic resin adsorbents) loaded with a variety of test adsorbates from aqueous solutions. The primary focus was on the adsorption of pesticides (e.g., Carbaryl, Alachlor, Atrazine, Pentachlorophenol, Trifluralin and Diazinon) with Alachlor and Atrazine in particular being selected for multicycle carbon adsorption-regeneration studies. These adsorbents showed a substantial decline in pesticide adsorption capacity after the first regeneration (30+%); Alachlor and Atrazine both exhibited a stable working capacity after several cycles.

This program included study of the adsorption of two other compounds, acetic acid and phenol, from aqueous solutions and subsequent supercritical carbon dioxide regeneration of the adsorbent. After eight adsorption-regeneration cycles with acetic acid adsorbate, there was no decline in carbon capacity. A number of types of GAC's and synthetic resins were used for multicycle tests with phenol. After initial declines of approximately 12 to 29 percent of virgin capacity, the regenerated adsorbents each reached their respective stable (steady state) working capacities at approximately 12 to 37 percent of virgin capacity.

This two-year program focused primarily on adsorbates sparingly soluble in the regenerating solvent. Another developmental program was begun to test the supercritical fluid regeneration process for adsorbates more soluble in the regenerant [5]. Chosen for study was the adsorption of volatile organic compounds (much more soluble in supercritical carbon dioxide than pesticide-like compounds) from a vapor stream onto (vapor-phase) granular activated carbon.

Volatile organic compounds (VOC's) studied in this program consisted of both leaded and unleaded gasoline vapors and ethanol and methyl ethyl ketone (MEK) vapors. The objective of the program was to study the use of supercritical carbon dioxide to regenerate carbon loaded with such vapors. Carbon adsorption has been a recognized method for the control of VOC emissions [5] but the principal drawback to its use was the decline of the carbon working capacity over multiple adsorption-regeneration cycles using various types of regeneration methods. The study showed that carbon loaded with gasoline, ethanol, or MEK vapors

could be completely regenerated by the supercritical carbon dioxide process over many cycles.

Other applications of supercritical carbon dioxide regeneration of adsorbents have been examined. In another program, samples of exhausted granular activated carbon loaded with trihalomethanes (THM) from a drinking water treatment process were regenerated with supercritical CO_2 [7]. After several adsorption-regeneration cycles, it was concluded that although conventional thermal regeneration of the GAC outperformed supercritical CO_2 regeneration, the supercritical CO_2 regeneration did reduce THM content to low levels in the adsorption column effluent and that a steady state capacity on the order of five to ten percent of virgin capacity could be obtained. Further investigation into process economics for both supercritical CO_2 and thermal regeneration methods was recommended so that a more detailed cost comparison of the two processes could be effected for a given specific performance.

Finally, an investigation was made into the use of supercritical carbon dioxide to regenerate spent polymeric resinous and carbonaceous resinous adsorbents [8]. Preliminary results indicate similar and, in some instances, better capacity recoveries for phenol and Alachlor using synthetic resins as compared with using GAC with the exception of one carbonaceous resin. Supercritical carbon dioxide regeneration of resin adsorbents was shown to be an alternative to capital and energy intensive thermal regeneration and expensive conventional solvent regeneration methods.

III. EXPERIMENTAL INVESTIGATION AND RESULTS

A. Experimental Evaluation

The experimental program was divided into two phases in order to evaluate the steady state performance of granular activated carbon in adsorbing contaminants from Rocky Mountain Arsenal wellwater.

In Phase I of the experimental program, three different commercially available GAC's (Calgon FS-400, Westvaco WV-G, Carborundum GAC-40) were compared in multicycle adsorption/regeneration tests. (The GAC's had similar characteristics but they were manufactured by three different companies.) Samples of each GAC from two-point adsorption isotherms were regenerated by the supercritical carbon dioxide process. A total of four adsorptions and three regenerations were performed for each GAC, resulting in three complete cycles. A five-point adsorption isotherm using pulverized virgin samples of each of the three carbons was done in order to confirm the two-point isotherms.

In Phase II of the experimental program, Westvaco WV-G was selected for a five adsorption/regeneration cycle test. Carbon from four-point adsorption isotherms was to be regenerated a total of five times, to complete five full cycles, in order to get a better idea of the steady state working capacity of the GAC for the contaminants. Both thermal regeneration method and supercritical carbon dioxide regeneration were to be compared.

Multicycle testing was terminated during the fourth cycle because the GAC was inadvertently contaminated with hydraulic fluid (oil) due to a pump diaphragm failure during the third supercritical regeneration.

All adsorption experiments were done on site at Rocky Mountain Arsenal by Rubel and Hager personnel and chemical analyses were performed by RMA lab personnel. Thermal regenerations were done by Westvaco Corp., Covington, Virginia. The supercritical regenerations were performed in laboratories at the Arthur D. Little, Inc., Cambridge, Massachusetts facility.

B. Equipment and Procedures

Adsorption Isotherm Testing Theory

The adsorption isotherm is a reliable laboratory procedure used to evaluate the applicability of adsorption for the removal of contaminants from water and other liquids. The data developed in these testing procedures describes the distribution of adsorbate in the solution and on the surface of the adsorbent. Freundlich adsorption theory relates this distribution of contaminant between solution and adsorbent surface by the following mathematical expression:

$$x/m = kc^{1/n}$$

where x = amount of contaminant adsorbed

m = weight of carbon

x/m = concentration in adsorbed state (i.e., the amount of contaminant adsorbed per unit weight of carbon)

c = equilibrium concentration in solution

k and n are constants

$\log x/m = \log K + 1/n \log c$

which is the equation of a straight line whose slope is $1/n$ and whose intercept is k at $c = 1$. Therefore, if s/m is plotted against c on log-log paper, a straight line should be obtained when testing the removal of low concentrations of contaminants from water.

Figures III-2 to III-7 of this report represent the Freundlich presentation of data obtained from adsorption isotherm testing.

Isotherm Testing -- Apparatus and Procedure

The apparatus used for the Phase I and II GAC adsorption isotherm testing study included two wrist-action shakers with a total capacity for sixteen one-liter flasks. Other laboratory apparatus included an analytical balance, vacuum filtration equipment and filters.

Prior to starting the isotherm tests, the granular activated carbon was dried in an oven at 105°C for 24 hours. For each isotherm point, eight hundred ml of water from RMA well number 23-120 was placed in a screw-top erlenmeyer flask. Into each flask was placed a known amount of GAC. Each adsorption test had a control: one additional flask without carbon. The flasks were placed on the shakers and agitated for 16-24 hours to insure complete adsorption equilibrium.

After agitation, the contents of each flask were filtered and the filtrate was sent to the laboratory at RMA for DIMP analysis. The filtered carbon from each test was dried at room temperature and shipped to Arthur D. Little for supercritical carbon dioxide regeneration (Phase I & II). Other GAC samples from the isotherm testing were thermally reactivated (Phase II only).

For Phase I, two isotherm points for the three different GAC's were done. The two carbon doses were 500 and 2000 mg GAC per liter of RMA wellwater. A five-point isotherm test with pulverized samples of each GAC was also done. In Phase II, four point isotherms were developed for the one type of GAC. The four carbon doses were 250, 500, 1000, and 2,000 mg GAC per liter RMA wellwater.

Thermal Regeneration Apparatus and Procedure

In order to evaluate the performance of the supercritical carbon dioxide regeneration process, conventional thermal regeneration was used as the experimental control.

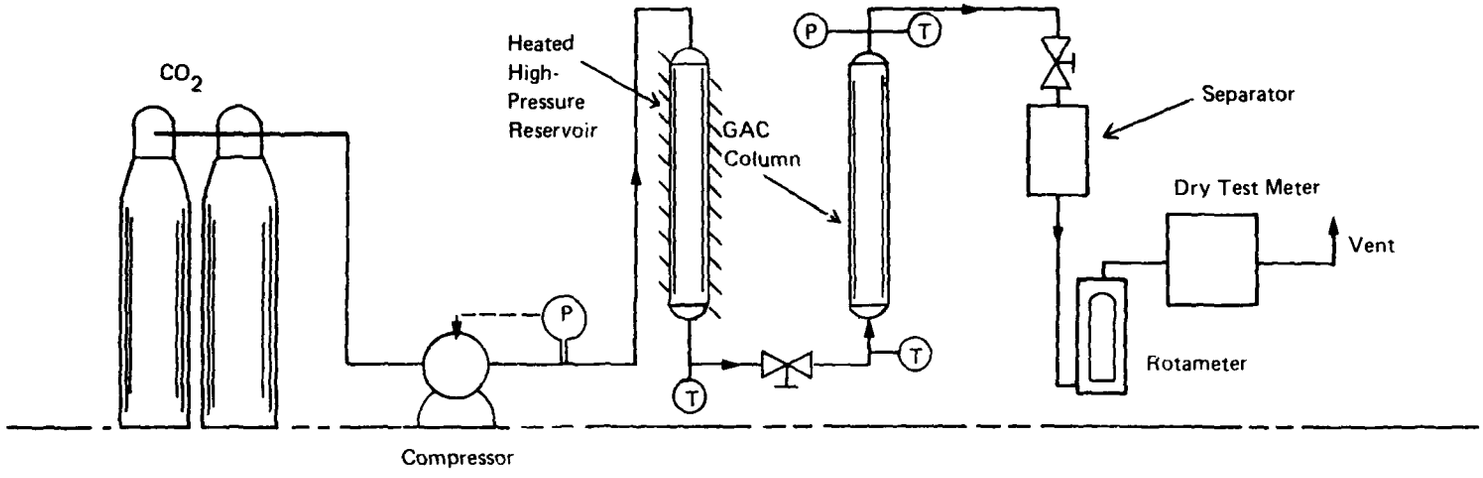
The apparatus used for the thermal reactivation (regeneration) of the GAC samples was an electrically-heated, three-zone tube furnace with manual feed and automatic temperature control (Lindberg Heavy Duty Equipment Company, tube 6.35 cm diam. x 60.96 cm long). The furnace temperature was maintained at 899°C (1650°F). Nitrogen and steam injection was used to maintain conditions similar to the actual atmosphere in a fossil fuel-fired thermal regeneration furnace. Regeneration times varied from fifteen minutes for the first regeneration to 2.5 minutes for the third regeneration indicating that the carbon was easy to regenerate.

Supercritical Carbon Dioxide Regeneration Apparatus and Procedure

A flow schematic of the experimental regeneration apparatus is shown in Figure III-1. Carbon dioxide (Cardox, 99.5%, with the balance N_2 and O_2 and with total hydrocarbon content, determined by flame-ionization detector, of 5 volume ppm of propane) was compressed from 58 atm to the regeneration pressure of approximately 214 atm with a diaphragm compressor (Superpressure, Inc., Model 46-13421) and heated to the regeneration temperature of approximately 130°C in the heat exchanger (high pressure reservoir) upstream of the regeneration column. The heated, pressurized stream was flowed at the rate of 5 SLPM (standard liters per minute) upflow through the GAC column for approximately ten hours. The CO_2 and any organics (such as DIMP) extracted from the GAC then flowed through the pressure letdown valve and into a cold trap. The trap, a packed 200 mm long glass U-tube immersed in solvent-dry ice bath maintained at -67°C, would collect organics or moisture which had separated from the gaseous CO_2 after the letdown valve. The carbon dioxide flowed out of the trap to a rotameter and dry test meter, to measure instantaneous flowrate and total CO_2 volume, respectively.

The regeneration column consisted of a section of one-inch O.D., medium pressure, 316 stainless steel tubing with high pressure fitting on each end (Autoclave Engineers, cat. nos. CNLX-16010, 20F41666). The high pressure reservoir was a 20-inch section of the same tubing. All other tubing, valves and fittings were 1/4" O.D., 316 stainless steel.

After regeneration, the GAC column was purged with compressed air to remove any residual carbon dioxide. The U-tube(s) containing the desorbate from Phase I, cycle 3 of the program were shipped to Atlantic Research Corporation for analysis. A copy of the report on the analysis of the desorbate is included in the Appendix, pages 54-63 [10]. The GAC was then shipped to RMA for readsorption.



Typical Regeneration Conditions:

P = 3100 PSI
T = 130°C
Q = 5 standard liters/min CO_2

FIGURE III-1 SCF CO_2 GAC REGENERATION APPARATUS

C. Results

Phase I -- Multicycle Tests with Three GAC Samples

The three carbons selected for multicycle tests with RMA wellwater were Calgon FS-400, Westvaco WV-G, and Carborundum GAC-40. Figure III-2 shows a set of five-point isotherms on pulverized, virgin samples of each GAC. Results indicate that the three carbons have very similar adsorption characteristics for DIMP as indicated by their similar isotherms. The loading on the GAC's at a DIMP concentration of 2,600 μg/l (2.6 ppm: the approximate concentration of DIMP in RMA well No. 23-120), is approximately 0.045 DIMP/g GAC for the Westvaco sample, 0.041 g DIMP/g GAC for the Calgon sample and 0.030 g DIMP/g GAC for the Carborundum sample. Figures III-3, III-4 and III-5 show multicycle two-point isotherms for the three supercritical CO_2 regenerated GAC's. As shown, there was a significant decline from virgin GAC capacity after the first regeneration cycle for all three carbons. With each subsequent cycle, the carbon underwent further decline, but not as large a decline as the original decline from virgin capacity. Because each isotherm is drawn from two-point plots, the accuracy may be low. Table III-1 gives the summary of the extrapolated multicycle carbon DIMP capacity (in equilibrium with the feed concentration of 2.6 ppm) for each GAC.

Upon examining the data, it was agreed that the adsorption performance of each of the three carbons with SCF CO_2 regeneration was essentially equivalent and that other characteristics of the carbon (i.e., mechanical characteristics) were essentially the same. None of the original three GAC samples had resisted attrition satisfactorily enough to be able to go an additional five cycles. Therefore, the decision was made to begin Phase II testing with fresh GAC. Carborundum GAC was ruled out because of a high ash content which might have had a detrimental effect on its thermal regenerability. The Westvaco GAC, which has adequate properties, was to be used in pulsed-bed adsorption testing at the North Boundary of RMA; Westvaco WV-G carbon was selected as the material of choice for testing in Phase II of the program [9].

Phase II -- Multicycle Tests with One GAC

Figures III-6 and III-7 present a set of four-point isotherms performed similarly to Phase I for multicycle carbon capacity measurements on Westvaco WV-G GAC. The isotherm samples were divided; half of the GAC then regenerated by SCF CO_2 and half by the thermal method. Only data from three cycles are valid because of the hydraulic oil contamination problem experienced during the third SCF CO_2 regeneration. Table III-2 shows a comparison of thermal versus SCF CO_2 regeneration performance at the DIMP feed concentration of 2.6 ppm based on the isotherms generated.

The data indicate that thermal regeneration restored the virgin carbon capacity for DIMP adsorption completely and that the GAC became more effective for DIMP adsorption following the first two regenerations. The measured apparent density of this GAC decreased with each reactivation:

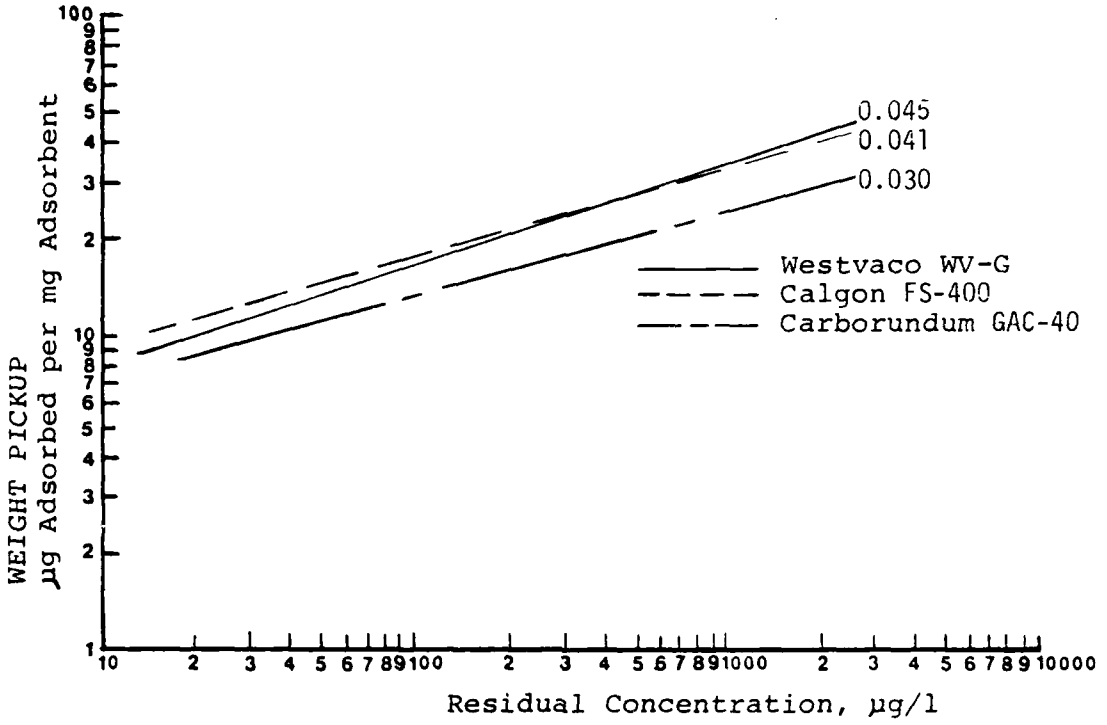


FIGURE III-2

PULVERIZED ACTIVATED CARBON ADSORPTION ISOTHERMS

DIMP ADSORPTION

Refer to data in Appendix, page 41

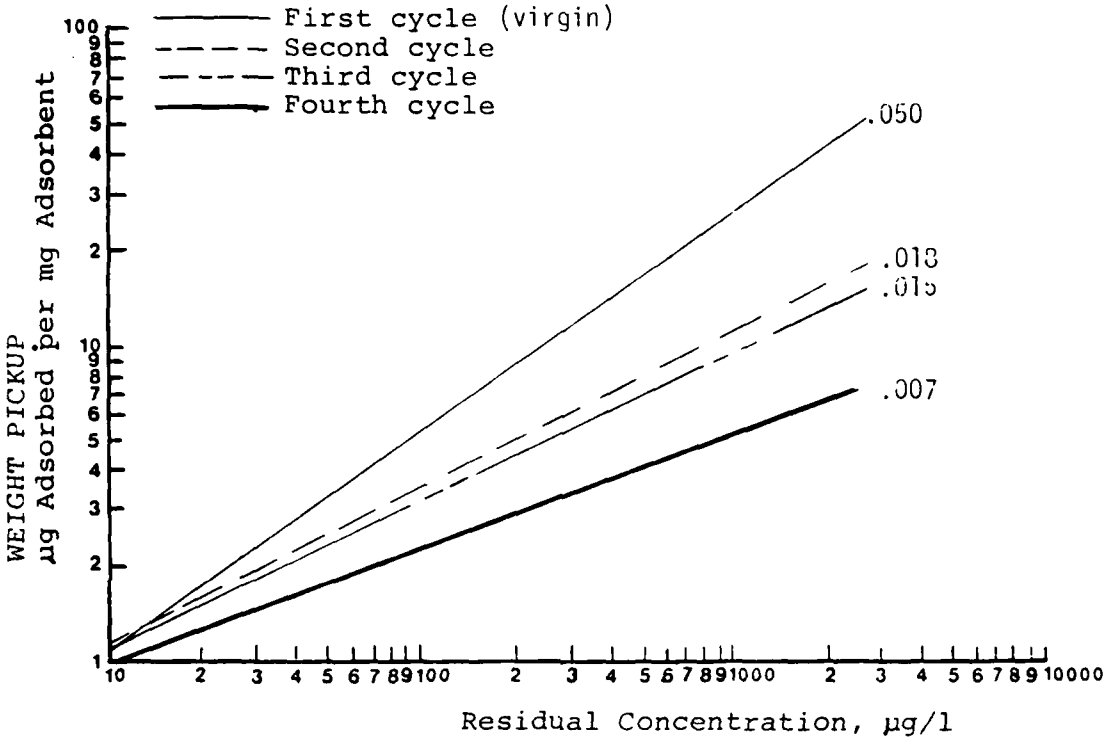


FIGURE III-3

GRANULAR ACTIVATED CARBON ADSORPTION ISOTHERMS

DIMP ADSORPTION

CALGON FS-400 12x40 mesh carbon

Refer to data in Appendix, Pages 42, 46

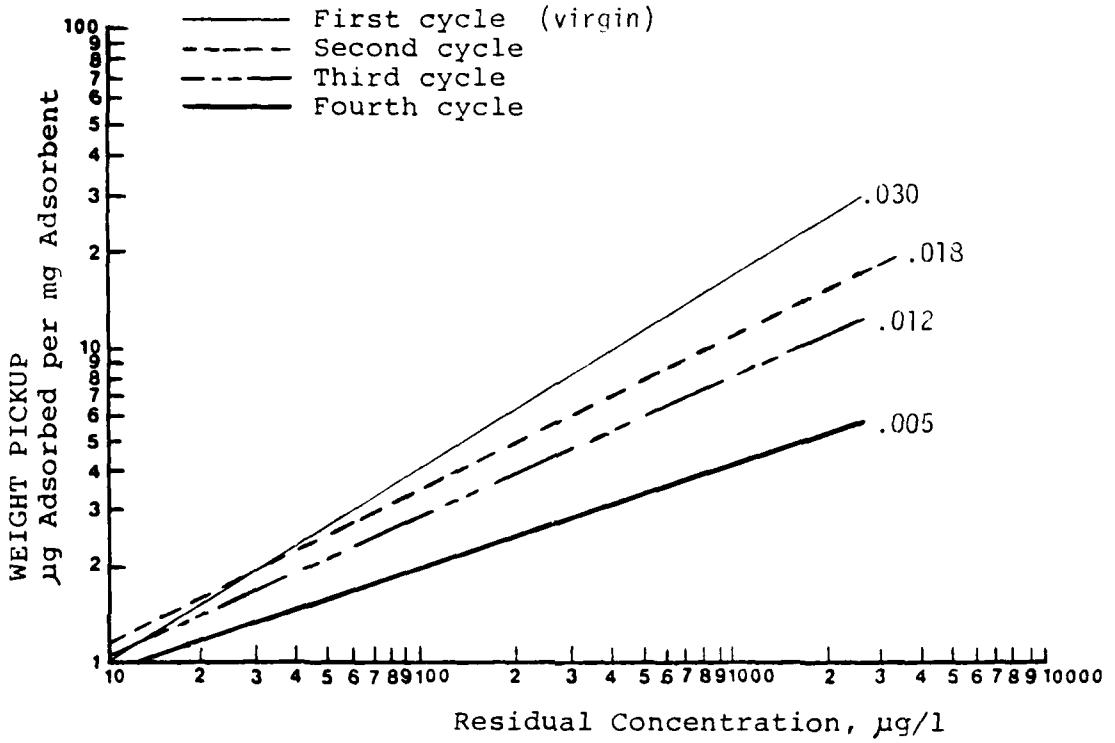


FIGURE III-4

GRANULAR ACTIVATED CARBON ADSORPTION ISOTHERMS

DIMP ADSORPTION

WESTVACO WV-G 12x40 mesh carbon

Refer to data in Appendix, Pages 42, 47

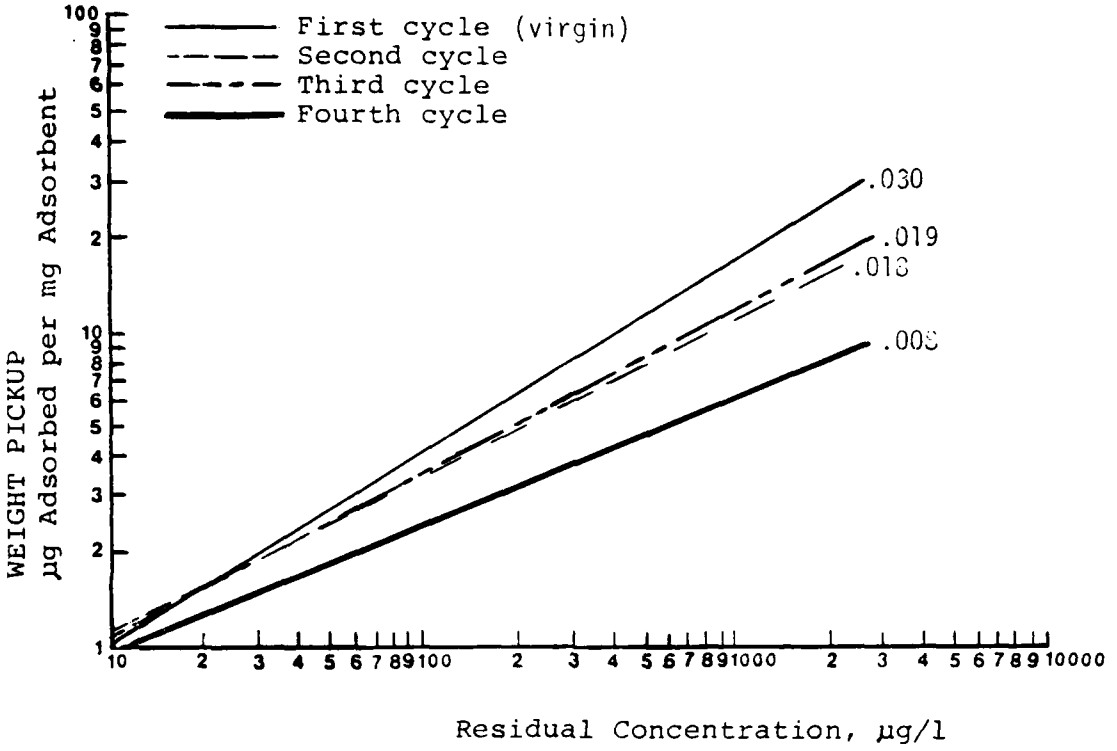


FIGURE III-5

GRANULAR ACTIVATED CARBON ADSORPTION ISOTHERMS

DIMP ADSORPTION

CARBORUNDUM GAC-40 12x40 mesh carbon

Refer to data in Appendix, Pages 42, 48

TABLE III-1

MULTICYCLE CAPACITY MEASUREMENTS OF DIMP ON GAC,
PHASE I DATA

Adsorption Number	Amount DIMP Adsorbed g DIMP/g GAC		
	FS-400	WV-G	GAC-40
1 (virgin)	0.050	0.030	0.030
2	0.018	0.018	0.018
3	0.015	0.012	0.019
4	0.008	0.006	0.008

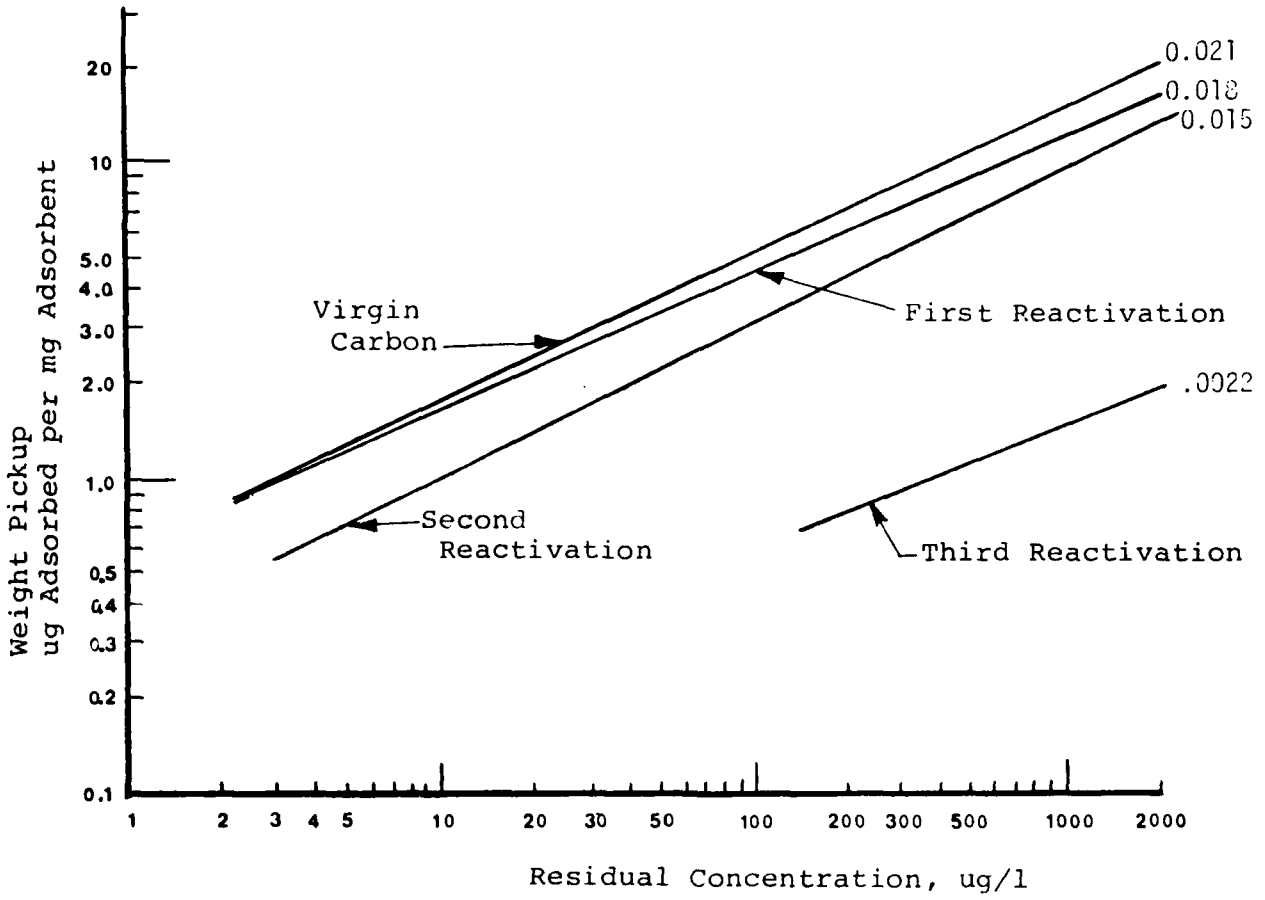


FIGURE III-6
GRANULAR ACTIVATED CARBON ADSORPTION ISOTHERMS
SUPERCRITICAL CO_2 REACTIVATED CARBON

Data from Page 43

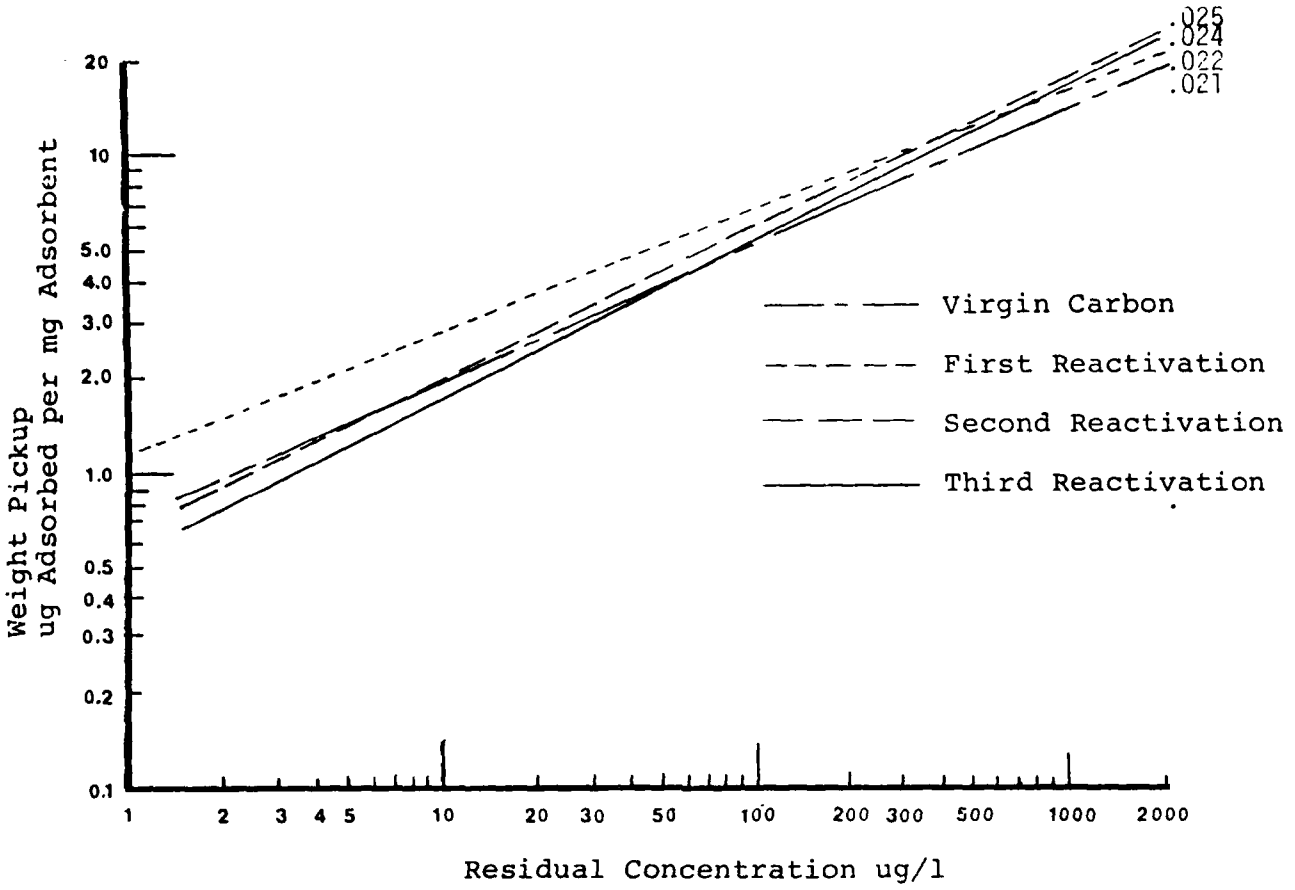


FIGURE III-7

GRANULAR ACTIVATED CARBON ADSORPTION ISOTHERMS
THERMALLY REACTIVATED CARBON

Data from Page 43

TABLE III-2

COMPARISON OF THERMAL AND SUPERCRITICAL CARBON DIOXIDE REGENERATION PERFORMANCE IN THE REMOVAL OF DIMP FROM WESTVACO WV-G

*Adsorption Number	DIMP Loading g DIMP/g GAC	
	Thermal	SCF CO_2
1 (virgin)	0.021	0.021
2	0.022	0.018
3	0.025	0.015
4	0.024	0.0022**

*Feed Concentration: 2.6 ppm DIMP

**Hydraulic Oil Contamination on SCF CO_2-Regenerated GAC

from 0.475 g/cc (virgin) to 0.446 (first reactivation), 0.43 (second reactivation), and 0.41 g/cc (third reactivation). These data indicate that the GAC was overreacted (overburned), probably because the GAC was exposed to the reactivation environment for too long a period. When small quantities of carbon (as used in this study) are reactivated in a laboratory furnace, control of the reactivation process is difficult and over-or-under reactivation may result. However, it is clear that the DIMP-loaded carbon is easily regenerated by conventional thermal methods.

Results for supercritical carbon dioxide regeneration showed approximately a twenty-eight percent DIMP capacity decline from virgin after three cycles of CO_2. Because of the hydraulic oil contamination, fourth and fifth cycle data were not obtained. An estimate of the final working capacity of the SCF CO_2-regenerated GAC was made for the economic evaluations. This estimate is 0.014 g DIMP/g GAC.

IV. PROCESS DESIGN AND ECONOMIC EVALUATION BASED ON LIMITED TEST DATA

Due to the limited data obtained and uncertainty of the data, the working capacity for SCF CO_2 regenerated carbon was estimated as closely as possible so that the process design and economic evaluation could be performed.

A. Preliminary Process Flowsheet and Design

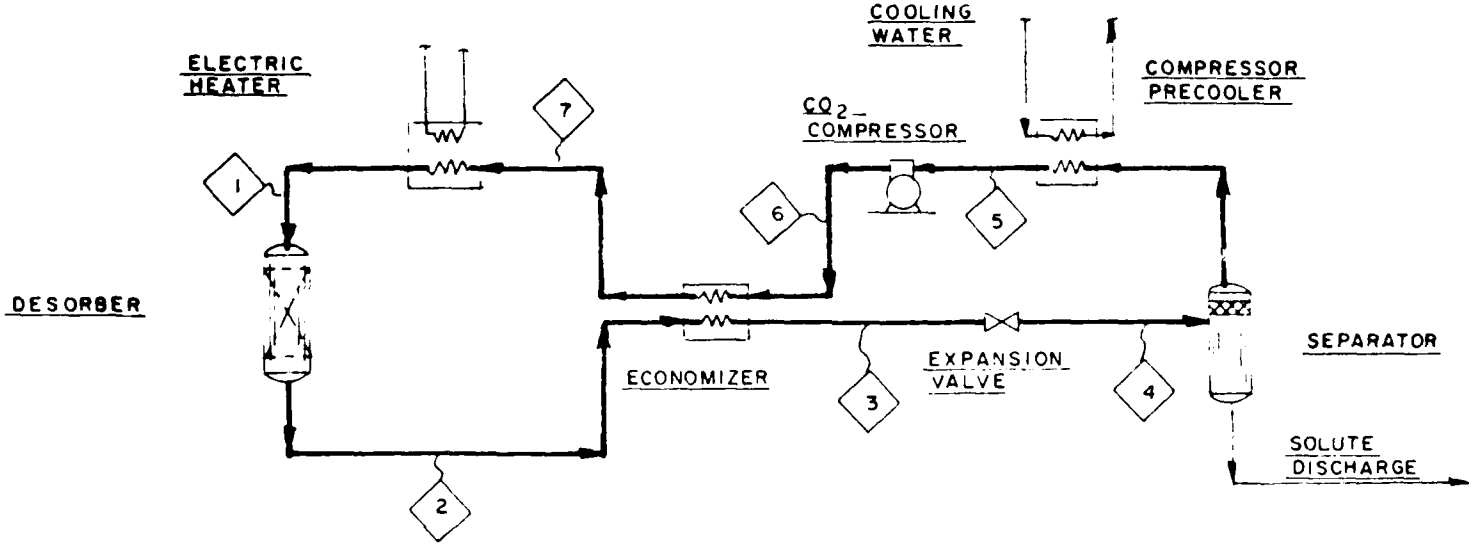
A simplified process flowsheet for a system to regenerate GAC loaded with DIMP and/or other contaminants is presented in Figure IV-1. A piping and instrumentation diagram for a typical supercritical carbon dioxide carbon regeneration plant is presented in Figure IV-2. The proposed process is outlined below.

GAC loaded with contaminants is charged to one of three high pressure desorption vessels from a spent carbon drain tank where the contaminants are desorbed from the GAC by contact with the SCF CO_2 (not shown). After desorption, the regenerated GAC is then slurried to a regenerated GAC hopper, (also not shown) and eventually back to the adsorption system. With respect to the carbon, this regeneration is considered a batch process.

The recirculating flow of supercritical carbon dioxide (SCF CO_2) passes through one of the regeneration vessels, where it removes a portion of the adsorbate from the GAC, and then is cooled in the economizer and reduced in pressure through the expansion valve. The cooling and reduction of pressure of the CO_2 through the valve significantly reduces its solubility for the desorbate, and the solute precipitates out of the CO_2 and is collected in the separator. The CO_2 flow from the separator is cooled, recompressed, heated in the economizer and electric heater, and recycled to the desorber. Thus, the CO_2 is recirculated continuously through the regeneration system.

Spent GAC is charged to and regenerated GAC discharged from the regeneration vessel(s) via a water slurry. Each desorber is equipped with a plate or screen assembly to allow drainage of superficial water. For design purposes, it is assumed that none of the water contained in the GAC pores is drained. The spent and regenerated GAC storage tanks are part of a standard adsorption system, and are not included as part of the regeneration plant.

CO_2 make-up is provided by cylinder liquid CO_2 at ambient temperature and its corresponding vapor pressure. A CO_2 charging tank is maintained at a pressure slightly above the compressor suction pressure. The charging tank is maintained full by flow from the low-pressure surge tank, and on demand by pressure control with flow from the make-up source.



STATE POINT	1	2	3	4	5	6	7
LOCATION	DESORBER INLET	ECONOMIZER INLET	EXPANSION VALVE INLET	SEPARATOR INLET	COMPRESSOR INLET	COMPRESSOR OUTLET	ELECTRIC HEATER INLET
CO_2 FLOW RATE kg/hr (lb/hr)	1590 (3500)	1590 (3500)	1590 (3500)	1590 (3500)	1590 (3500)	1590 (3500)	1590 (3500)
PRESSURE ATM (PSIA)	211 (3100)	211 (3100)	211 (3100)	88 (1300)	88 (1300)	211 (3100)	211 (3100)
TEMPERATURE °C (°F)	130 (265)	130 (265)	84 (183)	45 (112)	41 (106)	79 (174)	124 (255)

FIGURE IV-1 PROCESS FLOW DIAGRAM FOR THE REGENERATION OF ACTIVATED CARBON BY SUPERCRITICAL CARBON DIOXIDE: DIMP CASE

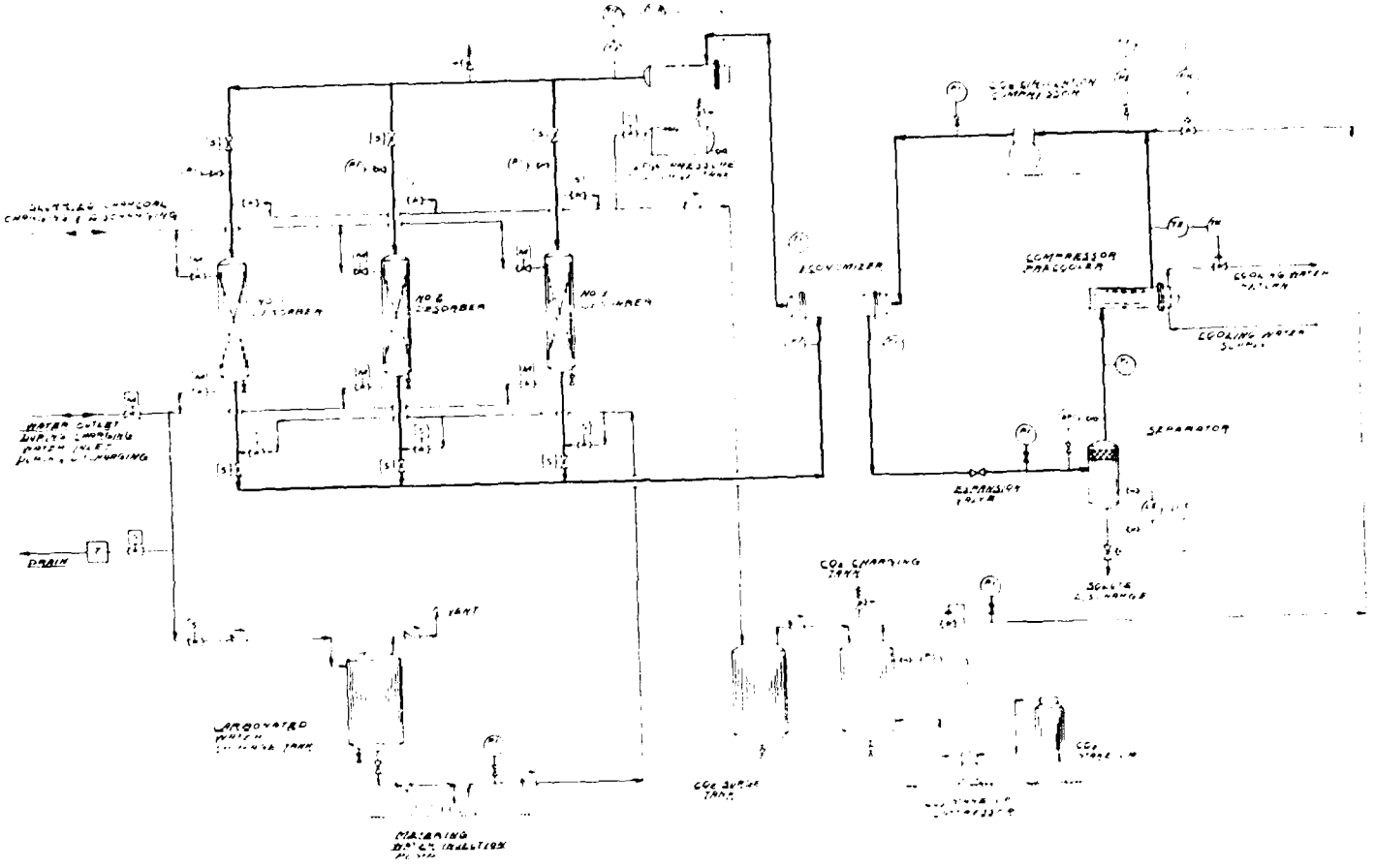


FIGURE IV-2 PIPING AND INSTRUMENTATION DIAGRAM
FOR SCF CARBON REGENERATION PROCESS

Make-up to the circulation loop is based on flow control at the compressor suction. A short-fall on recycle flow will open the make-up valve to allow CO_2 to be drawn from the make-up CO_2 charging tank.

The regeneration plant operates with one desorber on stream (for CO_2 circulation), and two desorbers involved in either charging or discharging carbon, or transferring CO_2 between them.

After a 30-minute regeneration cycle is completed in No. 1 desorber, flow is switched from No. 1 to No. 2 desorber. No. 3 desorber has been charged with spent carbon, and is completely filled with water to minimize introduction of air into the system. The high-pressure metering water pump then transfers carbonated water into No. 1 desorber at a low flow rate (sufficiently low to keep the bed from partly fluidizing), and slightly above bed pressure. The high-pressure water flow displaces CO_2 from desorber No. 1 to desorber No. 3, thereby pressurizing No. 3 bed to desorption pressure, and displacing its interstitial water. No. 3 desorber is then ready to accept CO_2 circulation for regeneration.

No. 1 bed, containing regenerated GAC in high-pressure water, and with pores containing high-pressure CO_2, is let down to separator pressure and held to allow expansion and release of a portion of the pore-volume CO_2. That CO_2 is collected in the low-pressure surge tank. No. 1 bed is then vented to atmospheric pressure, and the regenerated carbon is discharged as described above.

The same transfer and venting operation takes place at the completion of regeneration in each of the beds in sequence. Automatic valve operation is anticipated and accounted for in instrumenting an actual plant.

B. Process Economics

Table IV-1 lists the individual equipment components included in the supercritical carbon dioxide GAC regeneration system. In the past, Arthur D. Little has evaluated similar systems and has established a cost correlation between plant capacity (amount GAC processed per day) and initial capital cost [6][11].

SCF CO_2-regenerated carbon working capacity for DIMP of 0.014 g/g (or lb/lb) was used for the preliminary process evaluation. If a flowrate of 600 GPM (gallon per minute) of wellwater at 2.6 ppm DIMP is assumed, then approximately 19 pounds of DIMP would be removed per day. This corresponds to approximately 1400 pounds of GAC per day to be regenerated by the SCF CO_2 system. For a system this size, the total fixed system cost (including all equipment, installation, engineering, and contingencies) was estimated at $607,300.

Table IV-2 summarizes regeneration plant utilities, and Table IV-3 gives a summary of the SCF CO_2 regeneration plant operating costs on a daily basis. Because the plant was designed on the basis of a determined

TABLE IV-1

REGENERATION OF ACTIVATED CARBON BY SUPERCRITICAL CARBON DIOXIDE

List of Major Components

Case: DIMP: 1400 lb/day Regenerated GAC

1. Desorber assembly (3 required)
2. Carbonated water storage tank
3. Metering water injection pump
4. Low pressure CO_2 surge tank
5. High pressure CO_2 surge tank
6. CO_2 charging tank
7. Economizer
8. Separator
9. Compressor precooler
10. Circulation compressor
11. Heater
12. Valves
13. Instruments

Total capital cost estimated at
$607,300.00 (Dec. 1981 $)

TABLE IV-2

UTILITY REQUIREMENTS

Project: SCF CO_2 Regeneration of Activated Carbon

Case: DIMP
1400 lb/day of Regenerated Charcoal

UTILITY / EQUIPMENT	ELECTRICITY		COOLING WATER	
	CONDITION	QUANTITY	CONDITION	QUANTITY
Metering Water Injection Pump	460 V, 3 ph, 60 Hz	17 HP 12.7 KW Intermittent 2.6 min/Ø 40 Ø/day 22 KWH/day	-	-
Compressor Precooler	-	-	70 F Inlet 10 F ΔT	5.1 GPM Continuous 7.3 MGal/day
Circulation Compressor	460 V, 3 ph, 60 Hz	17.52 HP Continuous 13.07 KW 314 KWH/day	-	-
Electric Heater	460 V, 3 ph, 60 Hz	10.3 KW 121 KWH/day	-	-
Instrument & Control	-	1 KW 24 KWH/day	-	-
CO_2 Make-up Compressor	-	7 HP 5.22 KW 126 KWH	-	-
Total		607.0 KWH/day		7.3 MGal/day

NOTE: 1 MGAL = 10^3 gallons

TABLE IV-3

ESTIMATED PROCESSING COST OF ACTIVATED CHARCOAL REGENERATION BY SUPERCRITICAL CARBON DIOXIDE PROCESS

Plant Capacity: 1,400 lbs/day Regenerated Charcoal
Case: DIMP
Operating Factor: 330 days/year
Capital Investment: $607,300

Variable Costs	Unit/Day	$/Unit	$/Day
Electricity	607.7 KWH	0.05	$30.35
Cooling Water	7.5 MGal	0.11	0.80
Steam	- MMBtu	6.00	-
CO_2	140 Lbs	0.04	5.60
			$36.75

Semivariable Costs		
Operating Labor:	1/2 man/shift, 3 shifts/day @ $15/hr	$180.00
Supervision:	1/2 man @ $30,000/year	45.45
Labor Overhead:	60 Labor & Supervision	135.27
Maintenance:	3% of Capital Investment/year	55.21
		$415.93

Fixed Costs		
Plant Overhead:	40 of Labor & Supervision	$90.18
Taxes & Insurance:	2.0 of Capital Investment/year	36.81
Depreciation:	10 of Capital Investment/year	184.03
		$311.02

*Waste Disposal			
Incineration	1140 Lb/day	$800/2000 Lb	$456.00

Direct Processing Costs: $763.70/day
without waste disposal: $0.546/lb of Regenerated Charcoal

Direct Processing Costs with disposal
$1219.70/day
Incineration $0.871/lb of Regenerated Charcoal

*tentative figures for draft only.

steady state GAC working capacity after the decline from virgin capacity, carbon capacity losses are not a factor. Attrition losses are assumed to be small because they are normally associated with high temperature and solids mixing in regeneration furnaces. The estimated carbon processing cost is $0.546 per pound of regenerated carbon.

Waste Disposal

The supercritical carbon dioxide regeneration of GAC produces a desorbate concentrate of the contaminates being removed. Some amount of the pore water will also be soluble in the CO_2 so that the final separator product is a mixture of the desorbed organics and water. If this aqueous waste is hazardous or toxic, then it must be destroyed or sent to a controlled landfill. If the supercritical CO_2 process is to be compared with conventional methods of GAC regeneration, then the cost to dispose of waste must be added to the overall processing costs. This must be done as part of the comparative cost analysis because conventional thermal regeneration of GAC ultimately destroys (oxidizes) the desorbed species. Hazardous waste disposal engineers at Arthur D. Little, Inc. estimate that the price per ton (2000 lb) for the incineration of aqueous DIMP is $800.00 [12]. This results in an additional processing cost of $0.264 per pound of GAC regenerated for the case previously outlined.

Sensitivity of GAC Processing Costs to GAC Steady State Working Capacity

Table IV-4 presents a comparison of total processing costs of the SCF CO_2 carbon regeneration process for different carbon working capacities for DIMP. Capital and operating costs are compared for the base case (0.014 lb DIMP/lb GAC: 1400 lb GAC/day), for a working capacity of fifty percent higher (0.021 lb DIMP/lb GAC): 933 lb GAC/day) and for a working capacity of fifty percent lower (0.007 lb DIMP/lb GAC: 2800 lb GAC/day).

On the basis of cost per pound of DIMP processed, daily costs are not dramatically different for the three different working capacities. For relatively small SCF CO_2 GAC processing plants (less than 6,000 pounds of regenerated GAC per day) capital costs dominate, and variable costs (energy, cooling water, CO_2 make-up) which are more a function of GAC working capacity are a minor part of the total processing cost. Table IV-4 shows the relative magnitudes of the variable costs (directly related to steady state carbon capacity for the adsorbate) versus the semi-variable and fixed costs (more a function of labor and capital-related costs). Conversely, for large SCF CO_2 regeneration plants (greater than or equal to 10,000 pounds of regenerated GAC per day), capital-related costs become less dominant and variable costs are more significant to overall processing costs.

Therefore, the estimation of the GAC working capacity does not have a significant impact on the economics for the proposed SCF CO_2 GAC regeneration plant for RMA because of the relatively small plant size being considered.

TABLE IV-4

SENSITIVITY OF GAC PROCESSING COSTS TO GAC WORKING CAPACITY

GAC DIMP CAPACITY WEIGHT FRACTION OF GAC	0.021	0.014	0.007
PLANT CAPACITY LB/DAY	933	1400	2800
PLANT CAPITAL COST	$547,200	$607,300	$739,000
VARIABLE COSTS $/DAY	24.49	36.75	73.50
SEMI-VARIABLE COSTS $/DAY	410.47	415.93	427.90
FIXED COSTS $/DAY	289.16	311.02	358.91
TOTAL COST $/DAY	724.12	763.70	860.31
$/LB DIMP REMOVED WITHOUT DISPOSAL	$38.11	$40.19	$45.28

Thermal Regeneration Unit: Cost of Conventional GAC Regeneration Technology

The cost of thermally regenerating nine hundred pounds of GAC per day was estimated by comparison to past experience, and existing systems. Because the steady state working capacity for DIMP of thermally-regenerated GAC was shown to be 1.6 times that of GAC regenerated by SCF CO_2, less GAC per day would have to be thermally regenerated. Nine hundred pounds of GAC from thermal regeneration would have the equivalent performance of 1400 lb of SCF CO_2 regenerated GAC. Table IV-5 gives the daily total operating cost breakdown for a fossil fuel-fired, rotary kiln regenerating 900 pounds of GAC per day.

TABLE IV-5

ESTIMATED PROCESSING COST OF ACTIVATED CHARCOAL REGENERATION BY THERMAL REGENERATION

Plant Capacity: 900 lbs/day Regenerated Charcoal
Case: DIMP
Operating Factor: 330 days/year
Capital Investment: $150,000

Variable Costs	Unit/Day	$/Unit	$/Day
Electricity	90 KWH	0.05	4.50
Fuel	9 MMBtu	10.00	90.00
Steam	900 lb	0.05	45.00
Makeup GAC*	90 lb	0.75	67.50
			$207.00

Semivariable Costs		
Operating Labor:	1/2 man/shift, 1 shift/day @ $15/hr	60.00
Supervision:	1/2 man @ $30,000/year	45.45
Labor Overhead:	60% Labor & Supervision	63.27
Maintenance:	3% of Capital Investment/year	13.64
		$182.36

Fixed Costs		
Plant Overhead:	40% of Labor & Supervision	42.18
Taxes & Insurance:	2.0% of Capital Investment/year	9.09
Depreciation:	10% of Capital Investment/year	45.45
		$96.72

Direct Processing Costs: $486.08/day
$0.540/lb of Regenerated Charcoal

*Assume 10% loss due to burning.

V. CONCLUSIONS AND RECOMMENDATIONS

In this program, supercritical carbon dioxide regeneration of granular activated carbon loaded with DIMP from RMA wellwater was studied as an alternative to conventional thermal regeneration. Based on the results of experimental adsorption/regeneration studies, preliminary processes were proposed and an economic analysis prepared for both alternatives.

Conclusions

Test data indicated that the multicycle steady state working capacity of thermally-regenerated carbon for DIMP at its current concentration in RMA wellwater (2.6 ppm) was approximately 25 mg/g or 0.025 g/g (lb/lb). This capacity remained constant after three regenerations.

The data also indicated that the supercritical CO_2-regenerated carbon working capacity for DIMP at its current level of 2.6 ppm in RMA wellwater declined by approximately 28% of virgin carbon capacity after two regenerations. The capacity after 2 regenerations (3 cycles) was 15 mg/g or 0.015 g/g (lb/lb). A steady-state working capacity was estimated to be 0.014 g/g and this value was used in subsequent design calculations.

The sensitivity of preliminary SCF CO_2 process economics to the working capacity was examined and it was concluded that for the relatively small-scale process being evaluated, the overall effect of working capacity on the process economics was quite small.

Cost comparisons were made for each of the processes for a system to regenerate carbon loaded with DIMP. The adsorption system would treat approximately 600 GPM of DIMP-contaminated wellwater. Because of the difference in working capacities, the thermal process was designed to regenerate 900 pounds of GAC per day and the carbon dioxide process was designed to regenerate 1400 pounds of GAC per day.

The economic analysis and comparison leads to the following conclusions:

a) The direct processing costs on a daily basis were $486.08 and $1219.70 for the thermal and supercritical systems, respectively. These figures correspond to $0.56/1000 gallons wastewater for the thermal system and $1.41/1000 gallons wastewater for the supercritical system. Thus, the supercritical carbon dioxide process costs 2.5 times as much as the conventional system.

b) The initial capital cost of the carbon dioxide regeneration system is approximately four times the initial capital cost of the thermal system. Therefore, capital-related costs comprise a larger portion of the total daily operating costs for the CO_2 system than for the thermal system.

c) Variable costs, including energy-related costs, for the supercritical CO_2 process are $37.00 per day, while the variable costs for the thermal process are $207.00 per day, approximately five-and-one-half times higher.

d) Estimated labor-related costs for the two processes are quite different, the labor-related costs are about two-and-one-half times higher for the CO_2 process.

e) If virgin GAC were to be used and then disposed of (landfill) or destroyed (incinerated) instead of using regeneration, the approximate cost per day to treat 600 GPM of wellwater would be $1000.00 (landfill) to $1800.00 (destruction). These figures include the cost of the virgin carbon and various disposal costs.

f) The daily cost of the CO_2 regeneration system includes an $800.00/ton incineration cost for the desorbate. The thermal process (rotary kiln and pollution control equipment) is assumed to destroy the desorbed species.

The economic comparison shows that for the relatively small GAC treatment system required for the RMA application, supercritical fluid carbon dioxide regeneration cannot compete with conventional thermal regeneration.

Recommendations

Since the current state-of-the-art does not economically favor SCF CO_2 GAC regeneration for this application, the following areas are recommended for further investigation in order to reduce the cost and increase the efficiency of the SCF CO_2 process:

a) A system which could chemically oxidize the desorbed organics while still in the supercritical CO_2 would eliminate both the need for alternate disposal of the desorbate and the need for as large a pressure reduction in the system. This would reduce both capital and energy-related costs.

b) Examine the possibility of incorporating ultraviolet light (UV) catalyzed oxidation using peroxides or ozone in order to destroy the desorbate.

c) Other, less costly methods of destruction (other than incineration) of the desorbate should also be examined. Possibilities are supercritical water oxidation, biodegradation, etc.

d) Capital cost for the supercritical carbon dioxide system is relatively insensitive to GAC adsorption capacity. This implies that for larger-scale GAC applications, capital-related costs have less of an impact on the overall operating costs. Because variable (such as

energy) costs for the SCF CO_2 system are lower than for the thermal system, the SCF CO_2 alternative should become more economically feasible for large-scale carbon systems. Further investigation of this possibility is recommended.

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TABLE VI -1

RESULTS OF FIVE-POINT ISOTHERMS ON PULVERIZED GAC SAMPLES

RAW DATA PHASE I

	Sample No.	Adsorbent Dose (Mg/ℓ)	c_f [µg/ℓ]	$c_o - c_f$	X/M (µg DIMP ads/mg Adsorbent)
Carborundum GAC-40	1	0	2755		
	2	10.06	2472	283	22.5
	3	25.09	1851	904	28.8
	4	50.01	998	1757	28.1
	5	100.04	260	2495	19.9
	6	249.98	22.9	2732.1	8.74
Westvaco WV-G	7	0	2730		
	8	10.04	2295	435	34.7
	9	24.03	1545	1185	37.9
	10	49.92	650	2080	33.3
	11	100.24	116	2614	20.9
	12	249.84	15	2715	8.7
Calgon FS-400	13	0	2697		
	14	10	2484	213	21.3
	15	25	1814	883	35.3
	16	50	713	1984	39.7
	17	100	216	2481	24.8
	18	250	23.1	2674	10.7

From Pages 44 and 45

Data presented in Figure III-2, Page 13

TABLE VI -2

COMPARISON OF THREE GRANULAR ACTIVATED CARBONS

SUPERCRITICAL CO_2 REACTIVATION - GRANULAR CARBON ISOTHERMS

PHASE I RAW DATA*

CARBON	WT. CARBON grams	DIMP CONCENTRATION, mg/l			
		Virgin	1st React.	2nd React.	3rd React.
Westvaco WV-G	2.0	<10	<10	10.5	10.9
(P. 47)	0.25	255	480	626	1140
	0.0	2630	2780	2700	2450
Calgon FS-400	2.0	<10	<10	<10	<10
(P. 46)	0.25	182	450	621	901
	0.0	2630	2780	2700	2450
Carborundum					
GAC-40	2.0	<10	<10	10.9	<10
(P. 48)	0.25	256	445	418	786
	0.0	2630	2780	2700	2450

* Data from 800 ml volumes of water from RMA well 23-120.

TABLE VI -3

COMPARISON OF THERMAL VS SUPERCRITICAL CO_2

REACTIVATION OF GRANULAR ACTIVATED CARBON (1)

PHASE II RAW DATA

METHOD	WT. CARBON grams	DIMP CONCENTRATION, mg/l Virgin	1st React.	2nd. React.	3rd React.
THERMAL	0	2630	2710	2390	2307
Plotted in Fig. III-7 P. 20	2.0	2.6	0.1	3.5	3.4
	1.0	11.1	4.6	7.8	9.3
	0.5	99	28	29.3	30.1
	0.25	228	164	146	156
CO_2	0	2630	2380	2630	2244
Plotted in Fig. III-6 P. 19	2.0	3.1	2.44	14.0	256
	1.0	11.8	13.5	36.4	566
	0.5	55.3	49.4	182	(2)
	0.25	186	274	486	1694

(1) WESTVACO HG-40 12 x 40 Mesh

(2) value was measured as >500, actual value not available

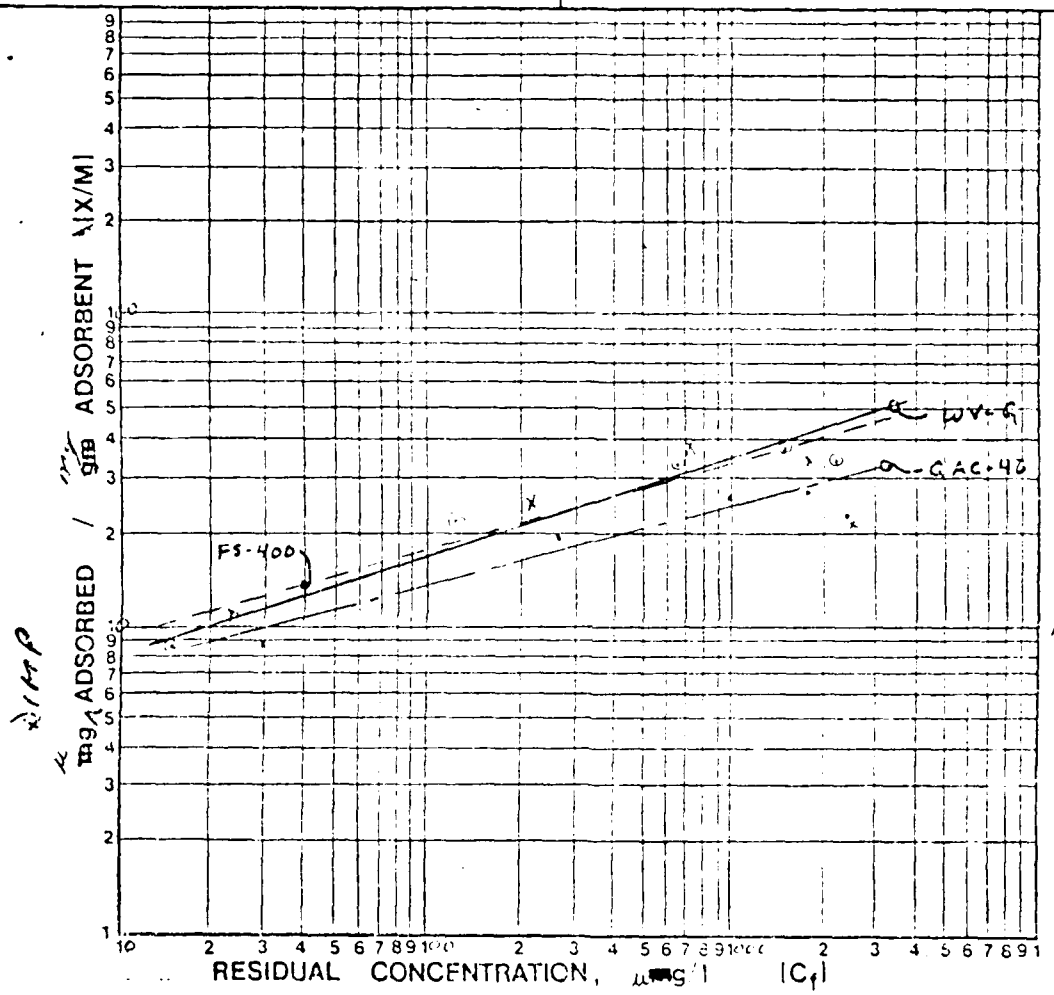
ADSORPTION ISOTHERM TEST DATA SHEET

RUBEL and HAGER, INC.
Consulting Engineers
4400 East Broadway
TUCSON, ARIZONA 85711

Location: WELL 23-120 Date: /
Investigator:
Remarks: 5 POINT - PULVERIZED

Client: RMA - A.D. LITTLE

DIMP



Plotted in Fig. III-2 P.13

Sample = GAC-40

pH Initial: 8.2 pH Treatment: 8.2
Temperature (°C): Room Agitation (rpm): 180

Bottle #	Adsorbent Dose (mg/l)	C_f Units:	$C_o - C_f$	X/M $\frac{C_o - C_f}{mg/l} \times 0.8$
0	0	2955		
1	10.06	2472	283	22.5
2	25.09	1851	904	28.8
3	50.01	998	1757	28.1
4	100.04	260	2495	19.9
5	248.48	22.9	2732.1	8.74

Sample = WV-G

pH Initial: 8.2 pH Treatment: 8.2
Temperature (°C): Room Agitation (rpm): 180

Bottle #	Adsorbent Dose (mg/l)	C_f Units:	$C_o - C_f$	X/M
10	[redacted] 0	2730		
11	[redacted] 10.04	2295	435	34.7
12	[redacted] 24.98	1545	1185	37.9
13	[redacted] 49.99	650	2080	33.3
14	[redacted] 100.24	116	2614	20.9
15	[redacted] 247.74	15	2715	8.7

Arthur D Little Inc

ADSORPTION ISOTHERM TEST DATA

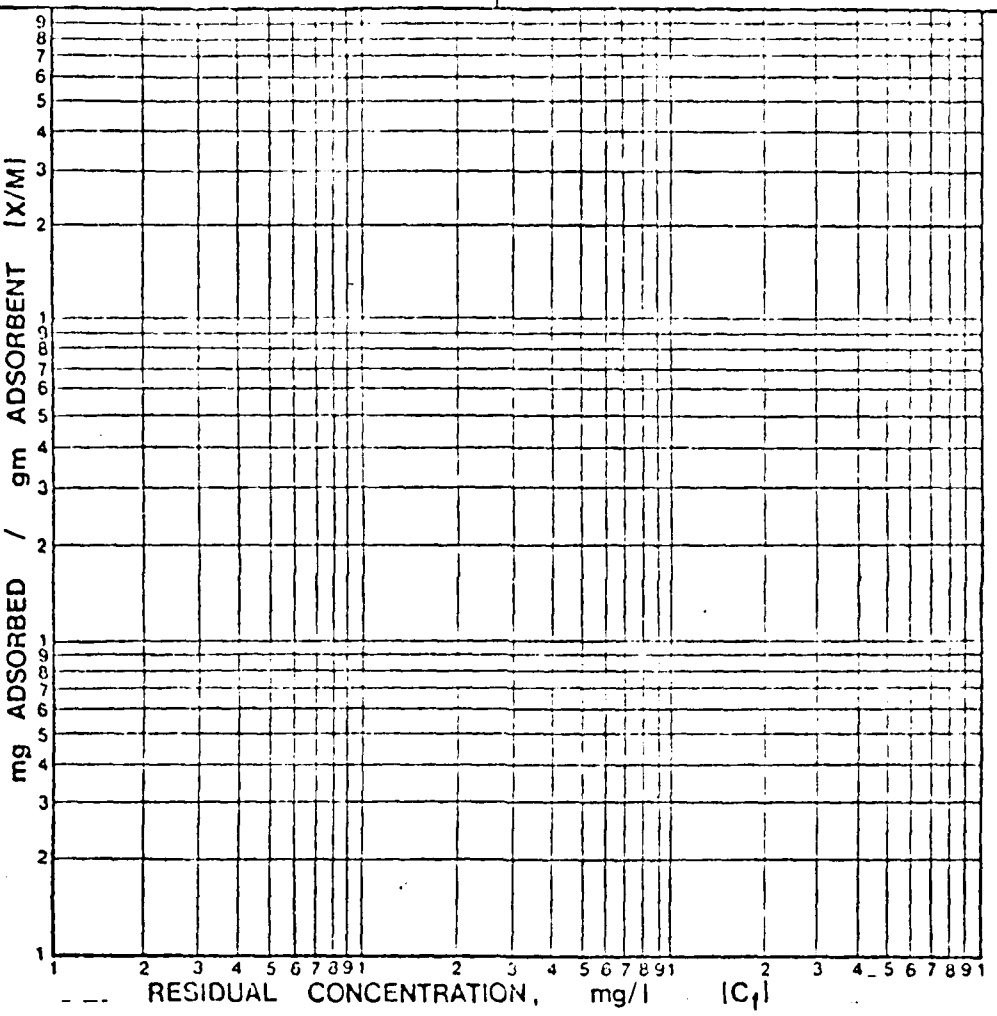
RUBEL and HAGER, INC.
Consulting Engineers
4400 East Broadway
TUCSON, ARIZONA 85711

Location : Date : /

Investigator :

Remarks :

Client :



Sample # FS-400

pH Initial : 8.2 pH Treatment : 8.2

Temperature [°C] : Room Agitation [min.] : 150

Bottle #	Adsorbent Dose [mg/l]	C_f Units :	$C_o - C_f$	X/M
20	0	269?		
21	10	248	21?	21.?
23	50	213	134	33.4
24	100	216	2481	24.8
25	150	23.1	2624	17.5

Sample #

pH Initial : pH Treatment :

Temperature [°C] : Agitation :

Bottle #	Adsorbent Dose [mg/l]	C_f Units :	$C_o - C_f$	X/M

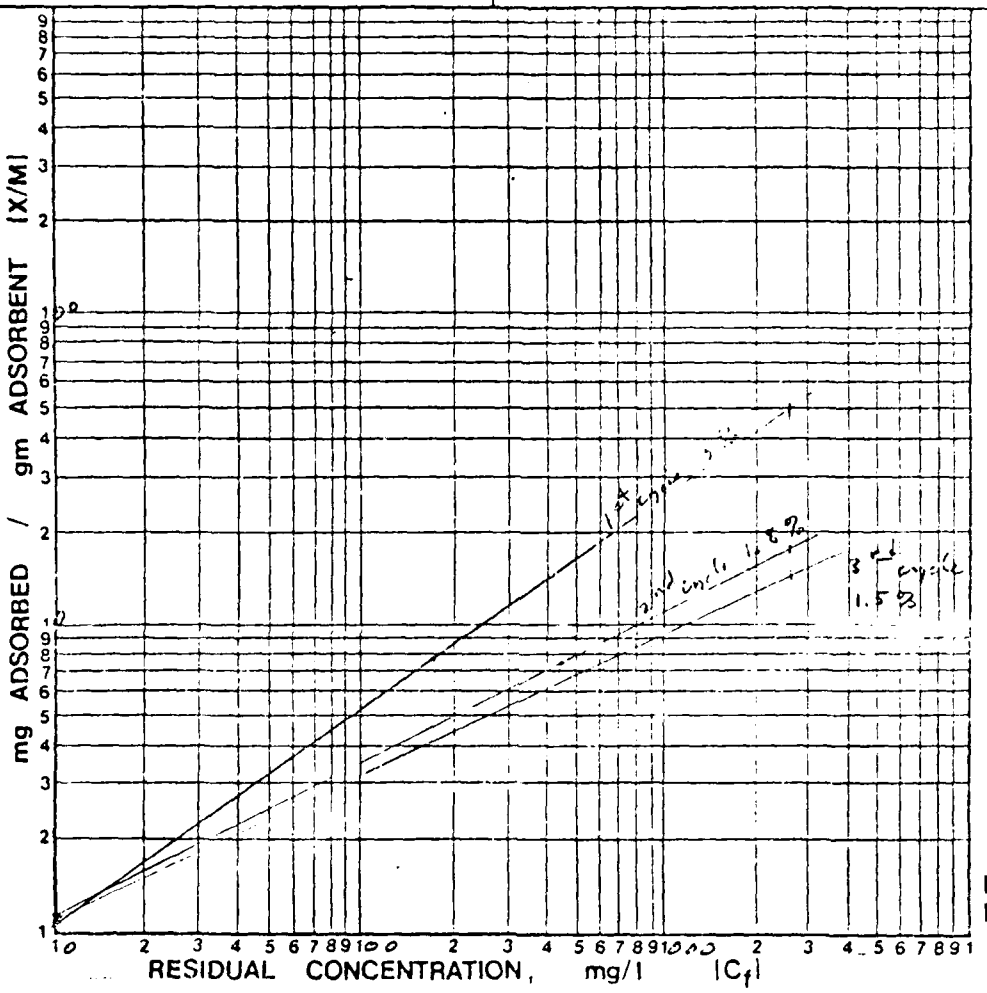
Arthur D Little Inc

ADSORPTION ISOTHERM TEST DATA

RUBEL and HAGER, INC.
Consulting Engineers
4400 East Broadway
TUCSON, ARIZONA 85711

Location: WELL 23-120 Date: /
Investigator:
Remarks: CALGON FS-400

Client: RMA - ADL



Plotted in Fig. III-3 P.15

Sample # CAL					Sample #				
pH Initial:		pH Treatment:			pH Initial:		pH Treatment:		
Temperature (°C):		Agitation (min.):			Temperature (°C):		Agitation:		
Bottle #	Adsorbent Dose (mg/l)	C_f Units:	$C_o - C_f$	X/M	Bottle #	Adsorbent Dose (mg/l)	C_f Units:	$C_o - C_f$	X/M
0	0	2630			0	0	2700		
5	2000	<10	2620	1.048	35	2000	<10	2690	1.076
6	250	182	2448	7.83	36	250	621	2079	6.65
23	0	2780			3	0	2950		
28	2000	<10	2770	1.108	a	2000	<10	2940	1.176
29	250	450	2330	7.46	b	250	901	2049	8.196

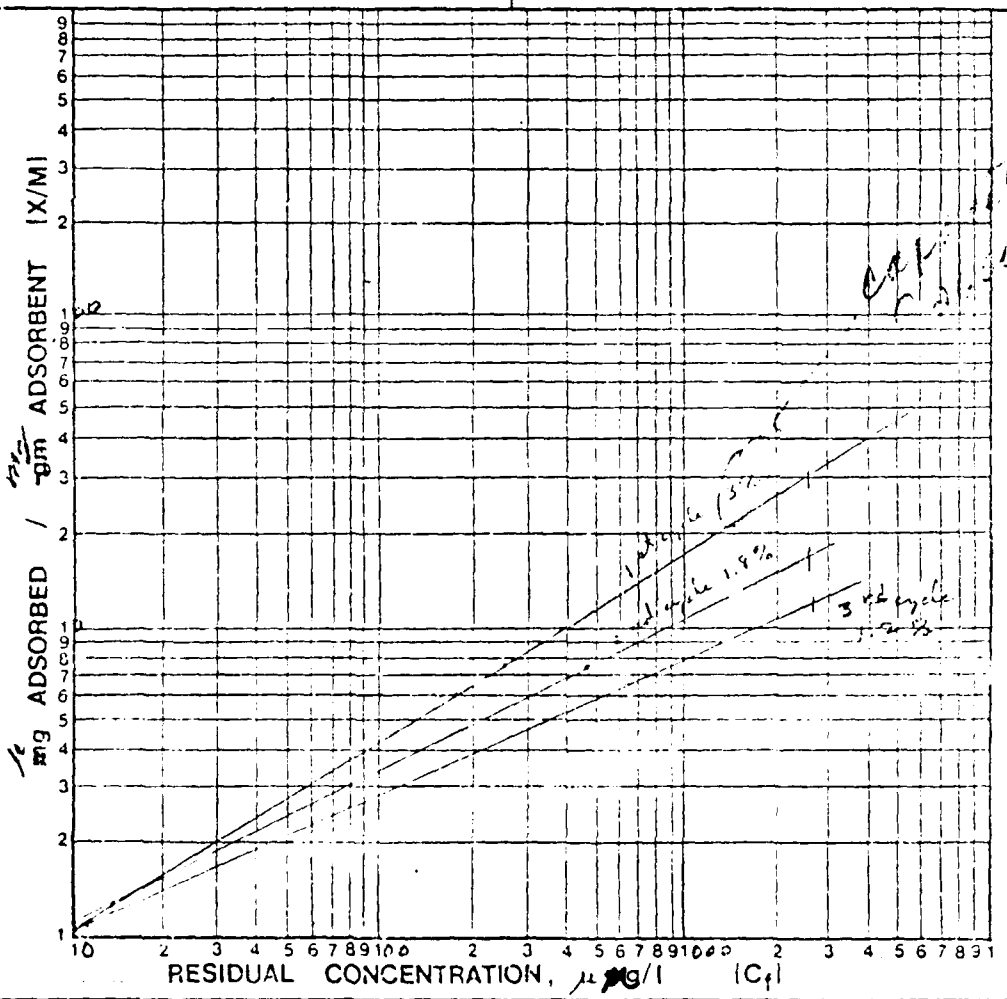
Arthur D Little Inc

ADSORPTION ISOTHERM TEST DATA

RUBEL and HAGER, INC.
Consulting Engineers
4400 East Broadway
TUCSON, ARIZONA 85711

Location: WELL 23-120 Date: /
Investigator:
Remarks: WESTVACO WV-G

Client: RMA - ADL



Plotted in Fig. III-4 P.16

Sample # 1st cycle WV-G					Sample # 3rd Cycle WV-G				
pH Initial:		pH Treatment:			pH Initial:		pH Treatment:		
Temperature (°C):		Agitation (rpm):			Temperature (°C):		Agitation:		
Bottle #	Adsorbent Dose (mg/l)	C_f Units: µg/l	$C_o - C_f$	X/M mg/g	Bottle #	Adsorbent Dose (mg/l)	C_f Units:	$C_o - C_f$	
0	0	2630	—		0	0	2700		
1	2000	<10	2620	1.048	31	200	10.5	2689.5	1.03%
2	250	255	2375	7.6	32	250	626	2074	61.4
	2nd cycle WV-G								
23	0	2782			1	1	2450		
24	2000	<10	2770	1.108			10.9	2.1	17%
25	250	480	2300	7.36			1100	1350	4

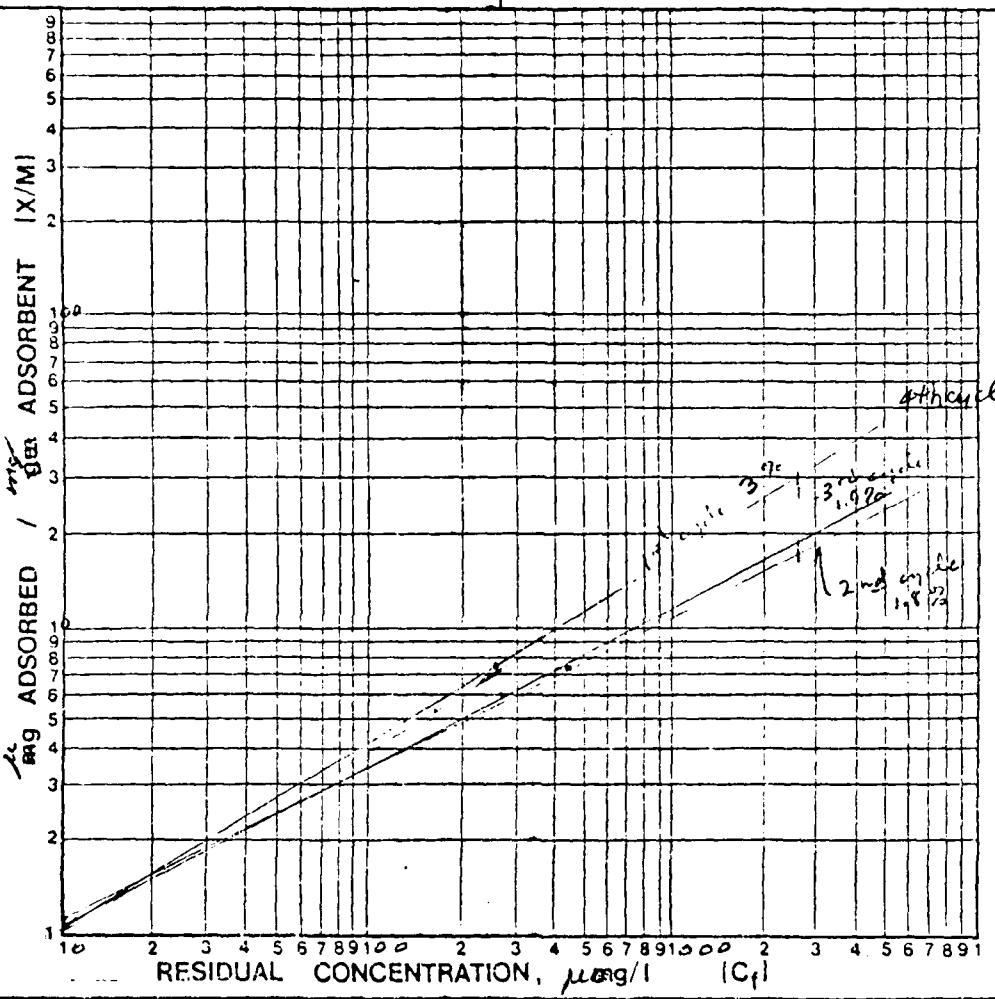
Arthur D Little Inc

AL ISOTHERM TEST DATA

RUBEL and HAGER, INC.
Consulting Engineers
4400 East Broadway
TUCSON, ARIZONA 85711

Location: WELL 23-120 Date: /
Investigator:
Remarks: CARBORUNDUM GAC-40

Client: RMA - ADL



Plotted in Fig. III-5 P. 17

Sample # GAC-40					Sample #				
pH Initial:		pH Treatment:			pH Initial:		pH Treatment:		
Temperature (°C):		Agitation (min.):			Temperature (°C):		Agitation:		
Bottle #	Adsorbent Dose (mg/l)	C_f Units: μg/l	$C_o - C_f$	X/M μg/mg	Bottle #	Adsorbent Dose (mg/l)	C_f Units:	$C_o - C_f$	X/M
0	0	2630	--		0	0	2700		
3	2000	<10	2620	1.049	33	2000	10.9	2689	1.076
4	250	256	2374	7.60	34	250	418	2282	7.3
23	0	2780			0	0	2450	-50	
24	2000	<10	2770	1.109	1	2000	<10	2440	1.176
27	250	445	2335	7.47	5	250	[illegible]	1[illegible]	[illegible]

Arthur D Little Inc

VII. APPENDIX

Raw Data (Regeneration) Phase I

CARBON TYPE: Westvaco WV-G

regeneration no.	250 mg dose	2.0 g dose
1	WV-G-L-1	WV-G-M-1
initial gac loaded	7.66 g	14.73 g
final gac returned	6.96 g	12.43 g
Δmass & gac loss	0.70 g	2.30 g
T	120°C	120°C
P	3000 PSIG	3000 PSIG
#SL	500 SL	880 SL
U-tube final	-	88.69
U-tube initial	-	88.30
Δmass U-tube	-	1.39 g
column before	-	708.30 g
column after	-	706.67 g
Δmass column	-	1.63 g
2	WV-G-L-2	WV-G-M-2
initial gac loaded	8.22 g	16.51 g
final gac returned	6.45 g	11.90 g
Δmass & gac loss	1.77 g	4.61 g
T	120°C	120°C
P	3000	3000
#SL	511	1118
U-tube final	78.69 g	96.18 g
U-tube initial	78.43 g	91.65 g
Δmass U-tube	0.26 g	5.31 g
column before	696.49 g	720.76 g
column after	694.71 g	716.21 g
Δmass column	1.78 g	4.55 g
3	WV-G-L-3	WV-G-M-3
initial gac loaded	7.03 g	12.94 g
final gac returned	5.77 g	9.73 g
Δmass & gac loss	1.26 g	3.21 g
T	120°C	120°C
P	3100 PSIG	3100 PSIG
#SL	623	1210
U-tube final	78.40 g	86.52 g
U-tube initial	78.30 g	82.31 g
Δmass U-tube	0.10 g	4.21 g
column before	-	709.48 g
column after	-	706.18 g
Δmass column	-	3.30 g

CARBON TYPE: Calgon FS-400

regeneration no.	250 mg dose	2.0 g dose
1	FS-400-L-1	FS-400-M-1
initial gac loaded	8.58 g	14.7 g
final gac returned	7.47 g	11.7 g
Δmass and gac loss	1.11 g	3.0 g
T	120°C	120°C
P	3000 PSIG	3000 PSIG
#SL	501	761
U-tube final	-	85.70 g
U-tube initial	-	83.35 g
Δmass U-tube	-	2.35 g
column before	-	700.64 g
column after	-	697.91 g
Δmass column	-	2.53 g
2	FS-400-L-2	FS-400-M-2
initial gac loaded	7.16 G	10.36 g
final gac returned	6.97 g	9.96 g
Δmass and gac loss	0.19 g	0.04 g
T	120°C	120°C
P	3000 PSIG	3000 PSIG
#SL	482	725
U-tube final	77.90 g	94.21 g
U-tube initial	77.84 g	96.96 g
Δmass tube	0.06 g	*(-)2.75 g
column before	710.51 g	700.70 g
column after	710.21 g	700.17 g
Δmass column	0.30 g	0.53 g
3	FS-400-L-3	FS-400-M-3
initial gac loaded	5.92 g	8.31 g
final gac returned	5.77 g	7.92 g
Δmass and gac loss	0.15 g	0.39 g
T	120°C	120°C
P	3100 PSIG	3100 PSIG
#SL	516	900
U-tube final	78.35 g	86.70 g
U-tube initial	78.40 g	86.52 g
Δmass U-tube	*(-)0.05 g	0.18 g
column before	696.50 g	701.22 g
column after	696.18 g	700.86 g
Δmass column	0.32 g	0.36 g

CARBON TYPE: Carborundum GAC-40

regeneration no.	250 mg dose	2.0 g dose
1	GAC-40-L-1	GAC-40-M-1
initial gac loaded	8.72 g	16.97 g
final gac returned	7.46 g	12.17 g
Δmass & gac loss	1.26 g	4.80 g
T	120°C	120°C
P	3000 PSIG	3000 PSIG
#SL	500	700
U-tube final	-	-
U-tube initial	-	-
ΔU-tube mass	-	-
column before	-	701.79 g
column after	-	697.22 g
Δmass column	-	4.57 g
2	GAC-40-L-2	GAC-40-M-2
initial gac loaded	10.22 g	19.43 g
final gac returned	6.92 g	12.09 g
Δmass and gac loss	3.30 g	7.34 g
T	120°C	120°C
P	3000 PSIG	3000 PSIG
#SL	670	1325
U-tube final	79.06 g	98.61 g
U-tube initial	77.90 g	94.21 g
ΔU-tube mass	1.16 g	4.40 g
column before	701.02 g	706.34 g
column after	697.84 g	699.23 g
Δmass column	3.18 g	7.11 g
3	GAC-40-L-3	GAC-40-M-3
initial gac loaded	7.51 g	16.39 g
final gac returned	6.42 g	11.46 g
Δmass and gac loss	1.09 g	4.93 g
T	120°C	120°C
P	3100 PSIG	3100 PSIG
#SL	1199	1240
U-tube final	78.31 g	94.42 g
U-tube initial	78.35 g	86.70 g
ΔU-tube mass	*(-)0.04 g	7.72 g
column before	696.80 g	706.43 g
column after	695.80 g	701.47 g
Δmass column	1.30 g	4.96 g

CARBON TYPE: Westvaco HG-40

regeneration no.	GAC from Combined Doses
1	HG-40-1
initial gac loaded	33.35 g
final gac returned	25.59 g
Δmass & gac loss	7.76 g
T	130°C
P	3100 PSIG
#SL	2470
U-tube final	82.34 g
U-tube initial	77.35 g
Δmass U-tube	4.99 g
column before	959.95 g
column after	952.08 g
Δmass column	7.87 g
2	HG-40-2
initial gac loaded	35.89 g
final gac returned	27.00 g
Δmass & gac loss	8.89 g
T	130°C
P	3100 PSIG
#SL	2439
U-tube final	90.63 g
U-tube initial	80.56 g
Δmass U-tube	10.07 g
column before	963.16 g
column after	954.43 g
Δmass column	8.73 g
3	HG-40-3
initial gac loaded	31.58 g
final gac returned	30.28 g
Δmass & gac loss	1.30 g
T	130°C
P	3100 PSIG
#SL	2219
U-tube final	**
U-tube initial	78.33 g
Δmass U-tube	-
column after	-
column before	958.20 g
Δmass column	-

Run terminated because compressor disabled.
Compressor hydraulic fluid contaminated sample of GAC tubing and U-tube.
Ran 150 SL propane to clean up oil from GAC followed by 2000+ SL CO_2.
Sent GAC back to RMA.

regeneration no.	GAC from Combined Doses
4	HG-40-4
initial gac loaded	32.57 g
final gac returned	24.46 g
Δ mass & gac loss	8.11 g
T	130°C
P	3100 PSIG
#SL	1786
U-tube final	84.57 g
U-tube initial	80.78 g
Δmass U-tube	3.79 g
column before	970.47 g
column after	955.38 g
Δmass column	15.09 g

Note - *run invalid because isotherm data for HG-40-4 showed little adsorption of DIMP.*

5	HG-40-5

run not done

*unexplained weight loss
**did not record final weight because tube contained small amounts of hydraulic fluid from compressor diaphragm failure.

ENGINEERING AND DEVELOPMENT SUPPORT OF GENERAL DECON TECHNOLOGY FOR THE DARCOM INSTALLATION RESTORATION PROGRAM

Task 8. Identification of Recovered Organics from Supercritical Fluid Process to Regenerate Carbon

FINAL REPORT

William E. Jones
Debra A. Price
Judith F. Kitchens

August 1981

Submitted to:

Commander
U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground (Edgewood Area), Maryland 21010

Ned Colburn
Project Officer

Contract No. DAAK11-80-C-0027

ATLANTIC RESEARCH CORPORATION
5390 Cherokee Avenue
Alexandria, Virginia 22314

A. Objective

The purpose of this task was to qualitatively identify the contaminants of Rocky Mountain Arsenal groundwater by GC/MS and compared the results to a GC/MS scan of the supercritical fluid extract of carbon provided by A.D. Litle. In addition to the qualitative analysis, a semi-quantitative analysis of the DIMP levels in both groundwater and carbon extract was performed.

B. Qualitative Analysis of RMA Groundwater

A 200 ml sample of the RMA groundwater was extracted with two 5 ml of ethyl ether. The extract was further concentrated to approximately 0.1 ml in a micro "Kuderna Danish" evaporator for GC/MS analysis. The chromatographic conditions were as follows:

Column:	2% Dexsil 300 on Anachrom Q
Oven Temperature:	140 - 200°C @ 15°C/minute
Injector Temperature:	200°C

Mass scanning was from 40 - 550 AMU at 8 samples per 0.1 AMU. An electron multiplier potential of 2,000 volts was employed.

The chromatogram of the groundwater extract gave two main peaks. The first gave a mass spectrum with major ions at 97 and 123 AMU. Comparison of this spectrum to that found for an authentic sample of DIMP established the identity of the peak. The second peak was tentatively identified as 2,6-di(τ-butyl)4-methylphenol by a manual search of the EPA/NIH Mass Spectral Data Base.

C. Analysis of A.D. Little U-Tube

As received from A.D. Little, the U-tube containing the supercritical extract from the carbon was wrapped in aluminum foil. Removal of the foil exposed a U-tube capped with teflon stopper. The tube had broken where the stopper was inserted but there was no evidence of loss of any of the tube's contents. The

tube contained about 4 - 5 ml of what appeared to be water. The tube contents were extracted by addition of two separate 5 ml portions of ether. The tube was recapped each time and shaken well before pouring out the contents. The combined extracts were separated from the water phase and injected directly without concentration. The U-tube extract showed the presence of only DIMP.

D. Semi-Quantitative Determination of DIMP Content in the RMA Ground Water and U-Tube

A second 100 ml sample of RMA groundwater was extracted twice with chloroform, the total extract amounting to 2 ml. Analysis was performed on a Hewlett Packard 5880 gas chromatograph equipped with a nitrogen phosphorous detector with the following conditions:

Column:	1.5% OV-17/1.95% OV-210	
Temperature:	Oven	130°C
	Injector	300°C
	Detector	320°C
Carrier:	N_2 @ 28 cc/minute	
Auxillary Gas:	H_2 @ 4 cc/minute	
	Air @ 90 cc/minute	
Sensitivity:	532 AU/ng (based on a 20.3 ng injection)	
Retention Time:	varies with sample size (0.8 - 1.5 minutes)	

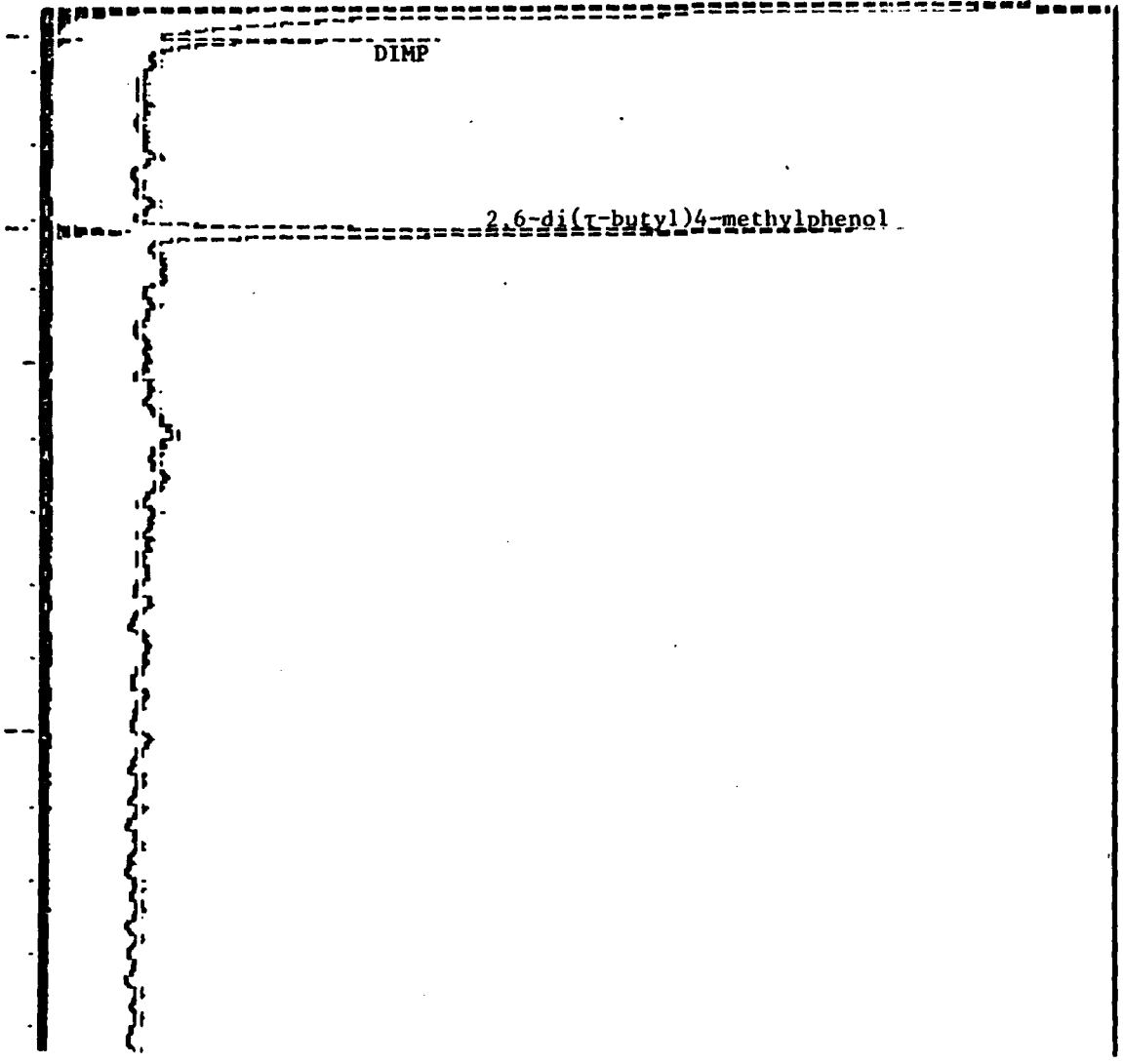
The RMA groundwater contained 1.55 mg/L of DIMP. The U-tube extract contained 31.47 mg/L of DIMP or a total 0.315 mg of DIMP. The efficiency of the supercritical carbon extraction can be determined if the amount of groundwater run through the carbon is known.

SAMPLE NAME WELL WATER EXTRACT (GC/MS)

OPERATOR

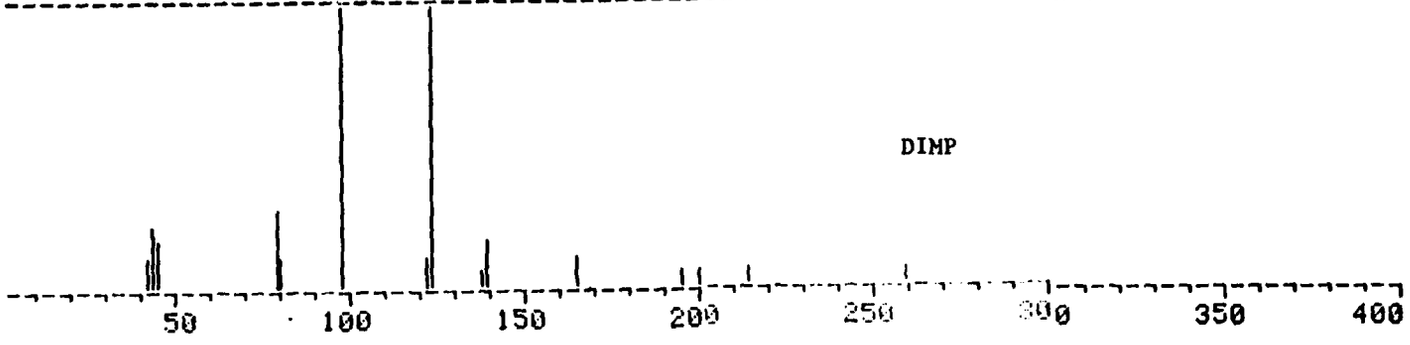
TOTAL ABUNDANCE FROM 40 TO 450 amu
Full Scale= 9920

ION 269.0
Full Scale= 150

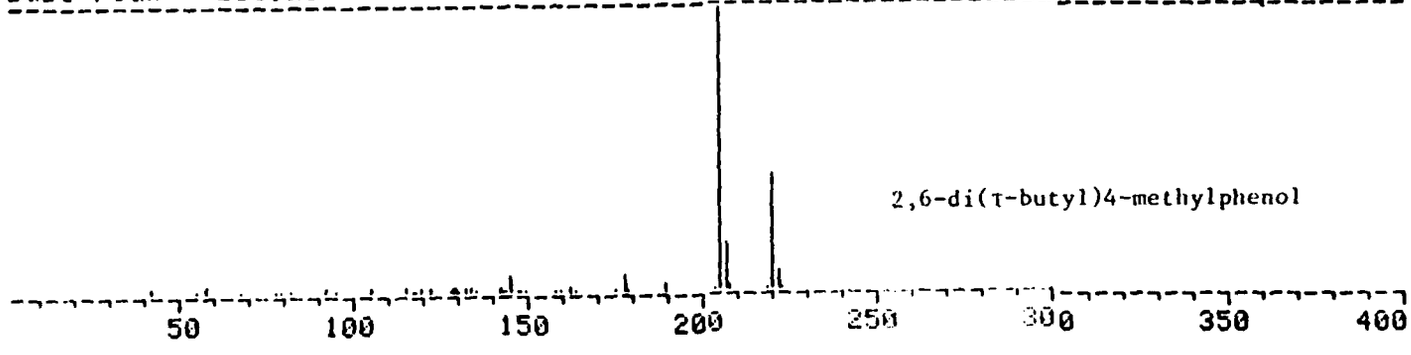


GROUNDWATER EXTRACT - MASS SPECTRA

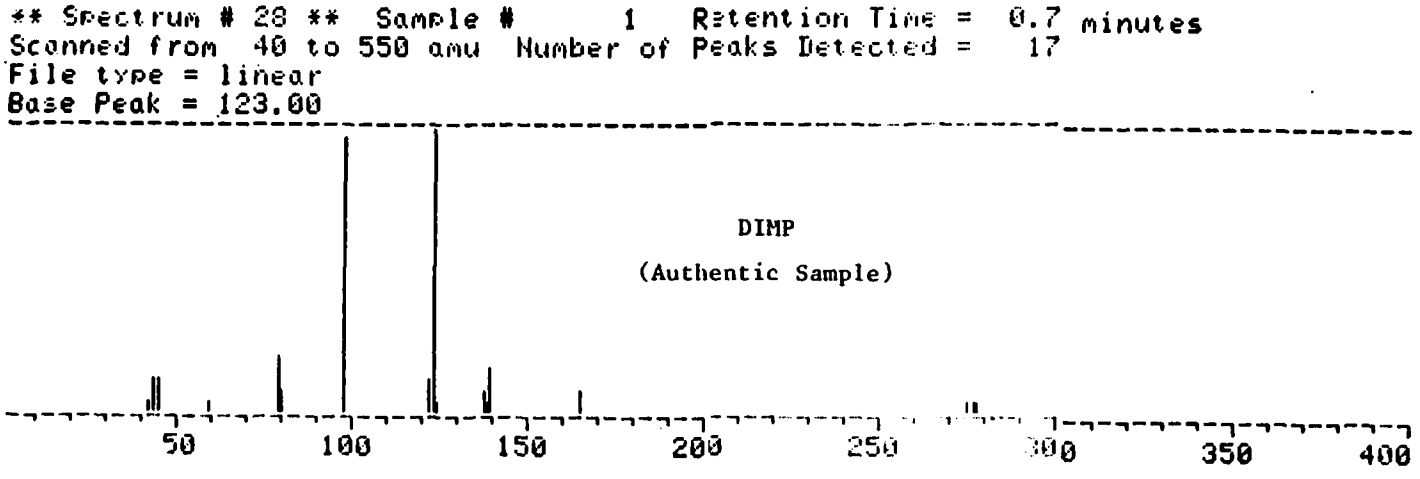
** Spectrum # 84 ** Sample # 1 Retention Time = 0.4 minutes
Scanned from 40 to 450 amu Number of Peaks Detected = 15
File type = linear
Base Peak = 96.95



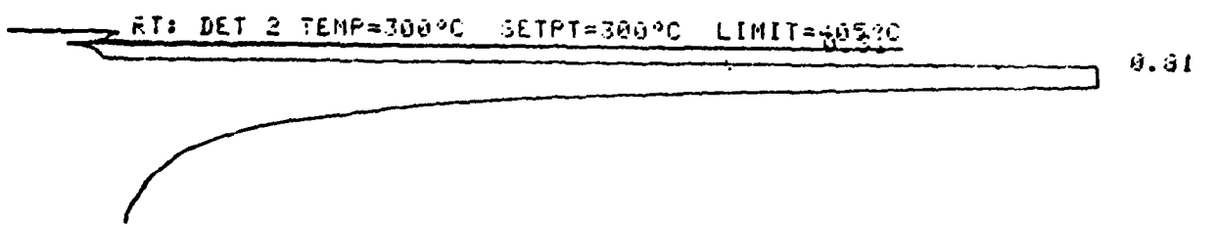
** Spectrum # 85 ** Sample # 1 Retention Time = 3.1 minutes
Scanned from 40 to 450 amu Number of Peaks Detected = 83
File type = linear
Base Peak = 205.20



DIMP - Mass Spectra



Chromatograph of Groundwater Extract

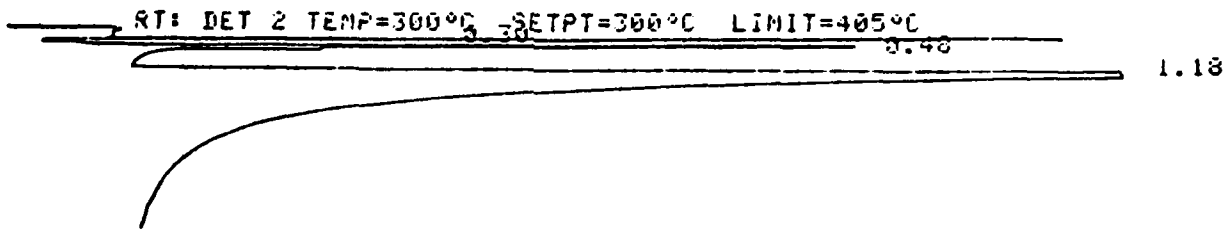


[MP] 5880A MANUAL INJECTION @ 14:30 AUG 7, 1981
AREA %

RT	AREA	TYPE	WIDTH	HEIGHT	BASELINE	AREA %
0.00			BASELINE @ START RUN = 48.28			
0.00			THRESHOLD @ START RUN = 1			
0.00			PEAK WIDTH @ START RUN = 0.08			
0.31	510.85	BP	0.024	334.27	33.48	0.646
0.81	78542.80	PB	*0.28 *	4453.97	28.75	99.354

TOTAL AREA = 79053.70
MULTIPLIER = 1

Chromatograph of U-Tube Extract



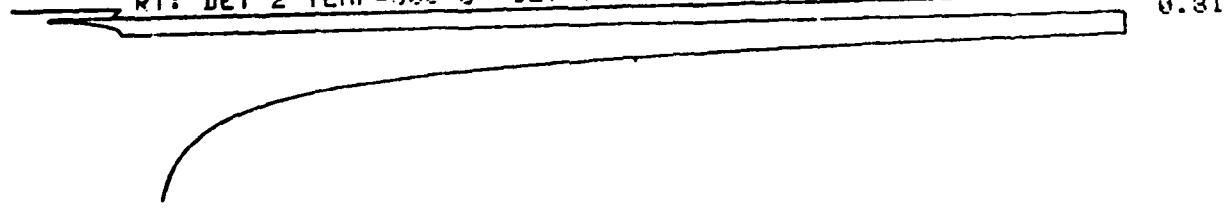
[illegible] 5080H ANNUAL INJECTION @ 14:17 AUG 7, 1981
AREA %

RT	AREA	TYPE	WIDTH	HEIGHT	BASELINE	AREA %
0.00			BASELINE @ START RUN = 37.61			
0.00			THRESHOLD @ START RUN = 1			
0.00			PEAK WIDTH @ START RUN = 0.08			
0.30	135.15	VP	0.012	175.34	5.47	0.381
0.48	2876.82	PH	*------*	376.91	0.94	8.115
1.18	32439.80	HH	------*	646.03	0.94	91.504

TOTAL AREA = 35451.80
MULTIPLIER = 1

Chromatograph of DIMP 77 ppm (SARM)

DIMP ANALYSIS OV17/OV21 COLUMN AT 130_C
RT: DET 2 TEMP=300°C SETPT=300°C LIMIT=405°C



[illegible] MANUAL INJECTION @ 13:41 AUG 7, 1981
AREA .

RT	AREA	TYPE	WIDTH	HEIGHT	BASELINE	AREA %
0.00			BASELINE @ START RUN = 35.65			
0.00			THRESHOLD @ START RUN = 1			
0.00			PEAK WIDTH @ START RUN = 0.08			
0.81	80947.10	PH	*0.36 *	3519.01	0.61	100.000

TOTAL AREA = 80947.10
MULTIPLIER = 1


FILMED
8-8